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# THE PHYSICAL REVIEW

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THE

# PHYSICAL REVIEW.

## STUDIES ON THE LOW-VOLTAGE ARC IN MERCURY VAPOR AND ITS RELATION TO FLUORESCENCE.

By Y. T. Yao.

Abstract.

**Low-voltage arc in mercury vapor.**—(1) *Variation of the striking and breaking voltages with conditions.* Using a simple tube, with incandescent tungsten filament as cathode and nearby mercury surface as anode, the arc was found to strike at voltages as low as 4.4 and to persist down to 1.8 volts, if the pressure was from 2–5 mm. and the cathode was sufficiently hot. (2) *Explanation.* If, however, correction is made for the initial velocity distribution of the electrons, the minimum electron energy necessary to maintain the arc comes out 5.5 volts which is the difference between the ionization potential, 10.4 volts, and the resonance potential 4.9 volts. Ionization is then effected by two successive mpacts, at 4.9 and 5.5 volts, in agreement with the theory of K. T. Compton. (3) *Effect of the absence of freshly distilled mercury vapor.* When a nickel anode was used and the mercury surface was removed to a considerable distance, 70 to 180 cm., the arc could not be maintained at a net voltage of 5.5, but 6.7 volts was required. This fact was demonstrated with three pieces of apparatus. This indicates that while freshly distilled mercury vapor, as is well known, is particularly active in fluorescent absorption of $\lambda$ 2536 radiation (4.9 volts), old vapor is more responsive to $\lambda$ 1849 radiation (6.7 volts).

**Correction for initial electron velocities in low-voltage arc measurements.**—The difference between the theoretical and observed minimum striking voltages, 2.5 volts for *sodium* (Wood and Okano) and 2.0 volts for *helium* (Compton, Lilly and Ohmstead), is doubtless equal to the voltage equivalent to the minimum initial energy of the electrons which start the arc. A table is given from which the proportion of electrons having energies above any value for any filament temperature may be computed.

### Introduction.

IN spite of the extensive work by various investigators[1] on low voltage arcs in metallic vapors, of which mercury is typical, the question as to whence comes the energy requisite to produce ionization at voltages less

[1] Hebb, Phys. Rev., 9, p. 371, 1917; 11, p. 171, 1918; 12, p. 482, 1918; McLennan, Proc. Phys. Soc. London, 31, p. 1, 1918; Tate, Phys. Rev., 10, p. 81, 1917; Tate and Foote, Phil. Mag., 36, p. 64, 1918; Rognley and Mohler, Phys. Rev., 13, p. 59, 1919; Foote and Meggers, Phil. Mag., 40, p. 80, 1920; and others.

than the minimum ionizing potentials remained unanswered until very recently. While the critical potentials at which the transition from elastic impacts of electrons with mercury molecules to inelastic ones takes place were proved by Franck and Hertz,[1] and later by Davis and Goucher[2], to be definite and determinative values given by the quantum law $eV = h\nu$, the existence of the single lined spectrum $\lambda$ 2536 to the exclusion of all others was questioned by Professor Millikan[3] from consideration of Kossel's relation. In the light of the then existing experimental data of Hebb,[4] Professor Millikan attributed the striking of the arc at a potential difference of about 5 volts to ionization by electrons emitted photoelectrically by the radiation $\lambda$ 2536, which is due to 4.9 volt impacts of the primary electrons. That the photoelectric effect is entirely inadequate to account for the observed phenomena was shown by Professor Compton.[5] Nor was Van der Bijl's[6] idea of direct successive impacts entirely successful, for then it would be necessary to assume that the atom could retain its resonance radiation for a length of time many times greater than would correspond to any value of this damping constant which has been found for any substance by direct experiment.[7,8] It was not until the theory of ionization by cumulative action of absorbed radiation and direct impact was proposed and developed by Professor Compton[9] in a series of papers that we have had an explanation of these phenomena which appears to be adequate.

Even then there was a great difficulty. In his recent work Hebb[10] has shown that an arc could be maintained in mercury vapor at as low as 3.2 volts, and in the work described below the lowest maintaining voltage reaches the value of 1.8 volts. Indeed, Hebb was led to doubt the fundamental importance attached to the point of 4.9 volts. It will be shown however, that the position which the point of 4.9 volts occupies in the electronic scheme of the mercury atom is in no way challenged by the maintenance of arcs at such abnormally low voltages; nor is it a fatal objection to the theory of ionization by cumulative action, *provided we take into account the distribution of the initial emission velocities of electrons*

[1] Franck and Hertz, Verh. d. Deutsch. Phys. Ges., 10, p. 457, 1913; 11, p. 512, 1914.
[2] Davis and Goucher, PHYS. REV., 10, p. 101, 1917.
[3] Millikan, PHYS. REV., 9, 378, 1917.
[4] Loc. cit., 1917.
[5] K. T. Compton, PHYS. REV., 15, p. 476, 1920.
[6] Van der Bijl, PHYS. REV., 10, p. 546, 1917.
[7] K. T. Compton, loc. cit.
[8] W. Wien, Ann. d. Phys., 60, p. 597, 1919; 66, 1921.
[9] K. T. Compton, PHYS. REV., 16, 282, 1920; Phil. Mag., 40, p. 553, 1920; PHYS. REV., 16, 501, 1920; Phil. Mag., 43, p. 531, 1922; and others in print.
[10] T. C. Hebb, PHYS. REV., 16, p. 375, 1920.

*from the incandescent source.* It is true that McLennan[1] did attribute the production of "faint arcs" below the minimum ionizing potential to the presence of abnormally high velocity electrons, but only when combined with the effect of absorbed radiation and direct impact does this give a satisfactory explanation.

If radiation plays such an important part in the production of ionization, as has been shown by the works of Professor Compton and his students[2] and of Horton and Miss Davies,[3] it is natural to assume that the conditions which are favorable for the excitation of radiation may also be favorable for the production of ionization. Now the necessary condition for fluorescence of mercury vapor has recently been shown by J. S. Van der Lingen and R. W. Wood[4] to be distillation; mercury vapor in static equilibrium with the metal, or when no liquid is present, does not exhibit fluorescence at any density or temperature. The persistence of fluorescence of mercury vapor in its active or freshly distilled state was observed early in 1914 by Philips,[5] and the time interval between absorption and emission of light in fluorescence has now been measured by Professor Wood.[6] Philips recorded that when the vapor in its stagnant state was excited by the line $\lambda$ 2536 the resonance radiation extended the width of the tube containing it. But as soon as distillation took place, the radiation became concentrated at the point where the exciting beam entered. A stream of green fluorescent light, originating from the concentrated patch of resonance radiation, passed round the tube with the distilling mercury vapor.

Since the radiation $\lambda$ 2536 is strongly absorbed by mercury vapor in vacuo at room temperature,[7] it seems that it does not depend on distillation. But that is not entirely convincing, for whenever the vapor is in contact with the fluid metal condensation and evaporation always take place. Perhaps we have this difference: While the few active entities present even in the quiescent state would suffice to produce resonance radiation of a detectable intensity, the number of such entities must be enormously increased in order to exhibit fluorescence. And this has been shown by the work of Van der Lingen and R. W. Wood,[8] who have recorded that with freshly distilled vapor, excited by the short wave-length spark line, the intensity of the emission line $\lambda$ 2536 is increased to sixty-fold its intensity in stagnant vapor.

[1] McLennan, Proc. Lond. Phys. Soc., 31, 1, 1918.
[2] Loc. cit.
[3] Horton and Davies, Phil. Mag., 41, p. 746, 1921.
[4] J. S. Van der Lingen and R. W. Wood, Astro. Phys. Jour., 54, p. 149, 1921.
[5] F. S. Philips, Proc. Roy. Soc. *A*, 89, p. 39, 1914.
[6] R. W. Wood, Proc. Roy. Soc. *A*, 99, 1921.
[7] R. W. Wood, Phil. Mag., 18, p. 240, 1909.
[8] Loc. cit.

In view of these facts and of the fundamental relation between radiation and ionization, it was thought that valuable information might be obtained if the low voltage arc phenomena were studied under identical conditions for the two cases: (1) When the vapor was very near the liquid surface, and (2) when it was far removed from it. The results are embodied in Part II. of this paper, Part I. being devoted to the study of the effect of the distribution of initial velocities of electrons.

## Part I. Effect of Initial Emission Velocities of Electrons on Minimum Ionizing Potentials.

### *Theoretical Considerations.*

In their derivation of the current voltage relation for thermionic currents from a hot cathode, both Child [1] and Langmuir [2] neglected the initial emission velocities of electrons. Richardson and Bazzoni [3] worked out the expression for currents in a gas with elastic electron impacts, and Professor Compton [4] has recently extended it for inelastic impacts. In all these cases the current is proportional to the 3/2 power of the voltage; they differ only in numerical constants and in the part which the mean free path of electrons plays. While the exact relation between current and voltage which takes account of the initial emission velocities requires further investigation,[5] we can see in a general way how it will affect the striking and maintaining voltages in the low voltage arcs.

The effect of space charge is, as we know, to limit the emission of electrons from the incandescent cathode and to change the uniform distribution of potential between cathode and anode. By applying Poisson's equation and on the assumption that the potential gradient is zero at the cathode, a solution is effected. But the emission of electrons with an initial velocity enables some of them to escape in spite of a negative potential gradient near the cathode, so that the surface of minimum potential and zero potential gradient is not at the cathode but a short distance from it. We shall assume that this minimum potential $\overline{V}$ measures the average initial energy of electron emission characteristic of the filament temperature. Accordingly, if $V_0$ is the true minimum striking voltage, by which we mean the difference between the ionization potential and the radiation potential (so that the sum of the energy absorbed from the radiation and that acquired from the impact may

[1] C. D. Child, Phys. Rev., 32, p. 492, 1911.
[2] I. Langmuir, Phys. Rev., 2, p. 450, 1913.
[3] O. W. Richardson and C. B. Bazzoni, Phil. Mag., 32, p. 426, 1916.
[4] Not yet published.
[5] See paper by W. Schottky, Phys. Zeit., 15, 1914.

equal the energy required for ionization), and if $V$ is the applied striking voltage, we have $V_0 - \overline{V} = V$. In the case of mercury $V_0$ is given by $V_i - V_r = 10.4 - 4.9$, or 5.5 volts. The observed striking voltage should be $V = 5.5 - \overline{V}$, where $\overline{V}$ depends on the temperature of the filament.

After the arc has struck, the condition changes in two essential aspects. In the first place, the presence of positive ions neutralizes the negative space charge and creates a positive space charge and thus greatly increases the electronic emission by enabling the saturation current to be approached or reached. In the second place the accumulation of positive ions near the cathode creates a "cathode fall," and facilitates the accumulation and ionization of molecules which are in an abnormal state due to absorption of radiation. As a consequence of the increase of total emission, the number of electrons having high velocities must be proportionally increased, although the mean kinetic energy characteristic of the cathode temperature remains the same.

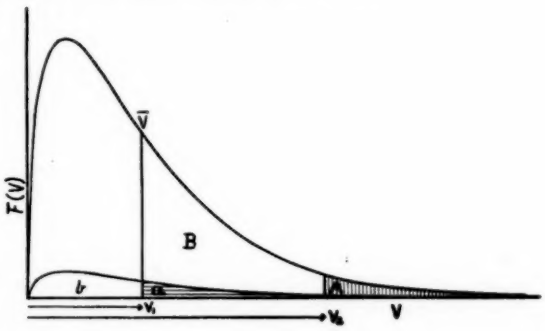



Fig. 1.

Let $b$ = total number of electrons emitted per second just before the striking of the arc; $a$ = the number of those electrons having speed $\geqq$ minimum speed for ionization equivalent to $V_0$, *i.e.*, the number of effective electrons required to cause the arc; $B$ = total number of electrons after the striking of arc; $A$ = the number of these electrons having speed $\geqq$ minimum speed for ionization equivalent to $V_0$, *i.e.*, the number of electrons required to maintain the arc.

Then, if $V_1$ is the initial velocity of electrons expressed in equivalent volts which, combined with the applied voltage $V$, would make up the required minimum potential for ionization $V_0$,

$$a = b\int_{V_1}^{\infty} F(V)dV = 2\pi b\left(\frac{e}{\pi kT}\right)^{3/2}\int_{V_1}^{\infty}\sqrt{V}\,\epsilon^{-\frac{eV}{kT}}dV \qquad (1)$$

and a similar expression holds for $A$, with the integration limit $V_2$.

On the assumption that it takes the same number of effective electrons to maintain the arc as to cause it, we have $A = a$.

Let $F$ = fraction $A/B$; $V_1 = \overline{V}$, whence $a/b = 0.39$, as given by the Kinetic Theory.

Then

$$F = 0.39\frac{b}{B}, \tag{2}$$

*i.e.*, 0.39 times the ratio of striking to maintaining currents.

From $F$ and $\overline{V}$, $V_2$ may be calculated by equation (1). Table I. gives solutions of equation (1) in a form for easy use. The mean energies $\overline{V}$ are twice those characteristic of gas molecules at the same temperature, in accord with the recent work of Sih Ling Ting.[1]

The results may be summarized as follows:

$$\begin{cases} V_0 - V = \text{striking voltage,} \\ V_0 - V_2 = \text{maintaining voltage.} \end{cases} \tag{3}$$

TABLE I.

| Filament Current (Amps.). | Temp. $K$. | $\overline{V}$. | $V_2/\overline{V}$. | $F$. |
|---|---|---|---|---|
| 15 | 2100 | 0.53 | 1.0 | 0.392 |
| 16 | 2270 | 0.57 | 1.5 | 0.217 |
| 17 | 2490 | 0.63 | 2.0 | 0.112 |
| 18 | 2620 | 0.66 | 2.5 | 0.062 |
| 19 | 2840 | 0.75 | 3.0 | 0.032 |
| 20 | 2970 | 0.80 | 3.5 | 0.0175 |
| 21 | 3150 | 0.83 | 4.0 | 0.0086 |
| 22 | 3270 | 0.88 | 5.0 | 0.0019 |
| 23 | 3470 | 0.90 | 6.0 | 0.00042 |
| 24 | 3570 | | 7.0 | 0.00011 |
| | | | 8.0 | 0.000027 |
| | | | 9.0 | 0.0000060 |
| | | | 10.0 | 0.0000014 |

The first two columns give the temperature of the filament cathode used in the following tests for various heating currents. The temperatures were estimated from the resistances, the small corrections due to the heavy leads being allowed for. $F$ is the fraction of the electrons emitted with energies equal to or greater than $V_2/\overline{V}$ times the mean energy $\overline{V}$.

## APPARATUS.

The apparatus for obtaining the arc is shown in the accompanying diagram. Its novel feature was that the liquid mercury itself formed the anode and the distance between it and the coiled tungsten filament was only about 5 mm. The bulb was made of G702P glass and connec-

[1] Sih Ling Ting, Roy. Soc. Proc., *A* 98, p. 374, 1921.

tion to a mercury diffusion pump was made by a side tube through a mercury cut-off. Before readings were taken, the liquid mercury was thoroughly boiled while the pump was kept in operation. Then the whole bulb and a part of the neck were immersed in a paraffin oil bath of large capacity, thus insuring the regulation of temperature and the supply of fresh mercury vapor. When a good vacuum was attained, as indicated by a McLeod gauge, the filament current was turned on and kept long enough to drive off any gases that might come out from it. Observations were made only at the best possible vacuum.

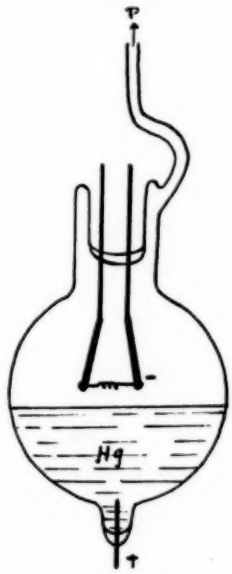


Fig. 2.

The accelerating field was regulated by series and parallel resistances and applied between the anode and the negative end of the filament, so that the voltmeter gave the largest voltage across the arc. The voltmeter reading, less half the voltage drop across the filament, gave the voltage drop between the anode and the middle of the filament. The filament was very short and coiled with three close turns in the middle. These coils, together with the conduction of heat away by the leads, made the central part of the filament much hotter than the rest, so that it behaved somewhat like an equipotential source. At very high temperatures, however, enough electrons may leave near the negative end of the filament to produce the arc. Thus the effective applied voltage should be counted to the middle of the filament at low temperatures, but to some point between the middle and the negative end at higher temperatures. The ionization current was measured by a microammeter with a series of shunts to accommodate it to currents of different sizes.

## RESULTS.

Preliminary experiments made at various vapor pressures indicated that the best temperature range for the striking of the arc at low voltages was 130° –150° C. although the actual vapor pressures must be somewhat higher than those indicated by the corresponding temperatures, since the hot filament was so close to the liquid surface. The following results were obtained within this temperature range.

Fig. 3 shows the relation between the current through the filament and the arcing voltage. (2) and (4) were plotted from experimental values of the striking voltages measured to the negative end and the

middle of the filament respectively. The correct value must be somewhere between these two limits, near the lower limit at lower temperatures and the upper limit at higher temperatures of the filament. The horizontal line (1) which cuts the ordinate at 5.5 volts indicates the

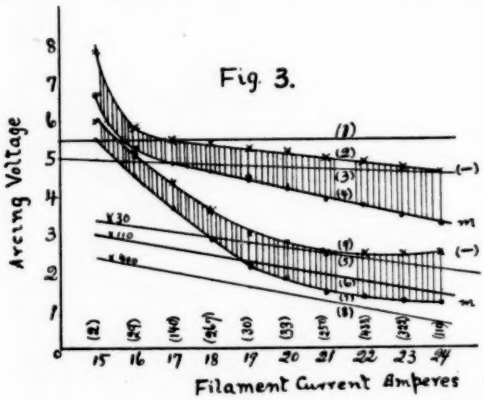



Fig. 3.

theoretical minimum ionization potential, if the electrons were all emitted with zero initial velocity. Curve (3) was obtained from (1) by subtracting the corresponding average initial energy characteristic of each temperature, according to equation (2) and Table I. It lies well within the limits of the experimental curves (2) and (4). The striking voltages at very small filament currents are abnormally high because the total bombarding electron current produces insufficient ionization to cause an arc except at velocities well above the critical minimum velocity.

The nature of the experimental curve is interesting in that it shows strikingly the point of transition characteristic of 4.9 volts. *The fact that the departure from a linear relation between the filament current and the arcing voltage sets in just at the point where the curve crosses the line of minimum ionization potential 5.5 volts in the descending order of abscissæ, is a convincing proof of the fundamental importance of the critical point of 4.9 volts.* Our results have, therefore, confirmed Hebb's findings and removed his objections.

In the case of maintaining the arc, the situation was not so simple. (9) and (7) were experimental curves, while (5), (6), and (8) were obtained from theoretical considerations developed in equations (2) and (3). The ratio of maintaining to striking currents at a particular striking voltage and for a given filament current was found experimentally to range from 30 to 400 as indicated by the numbers in brackets. Substituting any value within this range in equation (2), we get the fraction

$F$ of electrons having initial energy $\geqq V_2$. From Table I., $V_2$ can be estimated. The theoretical maintaining voltage was then obtained by taking the difference between the theoretical minimum ionizing potential 5.5 volts and $V_2$ according to equation (3). Curves (5), (6), and (8) show the maintaining voltages calculated thus for assumed current increases of 30, 110 and 400 fold above the pre-arc current. Since the pre-arc current is observed near a point of instability, the observed ratios of current increase are not very accurate, but fall within this range, as shown by the numbers in brackets. With a hot filament, the supply of electrons is adequate, and it is seen that the observed low maintaining voltages agree with those predicted from considerations of velocity distribution as well as can be expected.

A study of the relation between the voltage across the arc and the current through it reveals a very interesting feature. If, after the arc has struck, the series resistance is decreased, the potential across the arc decreases, while the current increases. Beyond the lowest maintaining voltage it begins to rise again with continually increasing current. On increasing the series resistance and therefore diminishing the applied field, the arc potential decreases to exactly the same lowest maintaining voltage, and then rises again, while the current continually decreases. The arc breaks at precisely the same point as where it strikes. The process is perfectly reversible. This phenomenon of reversibility was also observed by Compton, Lilly, and Olmstead[1] in a certain case of the low voltage arc in helium. In the present case the current-voltage changes are always reversible provided the filament is hot enough to cause the arc to strike at a voltage $5.5 - \overline{V}$, although the change immediately following the striking or preceding the breaking of the arc is discontinuous except at very high filament temperatures. If the filament is too cool to permit an arc at a voltage $5.5 - \overline{V}$ (as at 15 amperes in Fig. 3), the arc strikes at a higher voltage but may break at $5.5 - \overline{V}$ volts, and is therefore not reversible in this case.

Fig. 4 is an example among a large number of sets of observations made at various filament temperatures. Curves (1) and (2) show experimental maintaining voltages and currents, the voltages being taken to the negative end and middle of the filament, respectively. The shaded area, therefore, sets the experimental limits within which the true value should lie. The curve (3) was obtained as before from consideration of the initial energy and the increase of electronic emission after the arc struck. Again the agreement is within the probable limits of error. That the theoretical curve departs widely from the experimental curve

[1] Compton, Lilly, Olmstead, PHYS. REV., 16, p. 282, 1920.

after the point of the lowest maintaining voltage is reached is explained by the fact that it is based upon the assumption of an unlimited supply of electrons, whereas, in the actual case, a state of saturation is approached at the lowest maintaining voltage, and, therefore, a higher potential must be applied in order that more electrons may get across the arc.

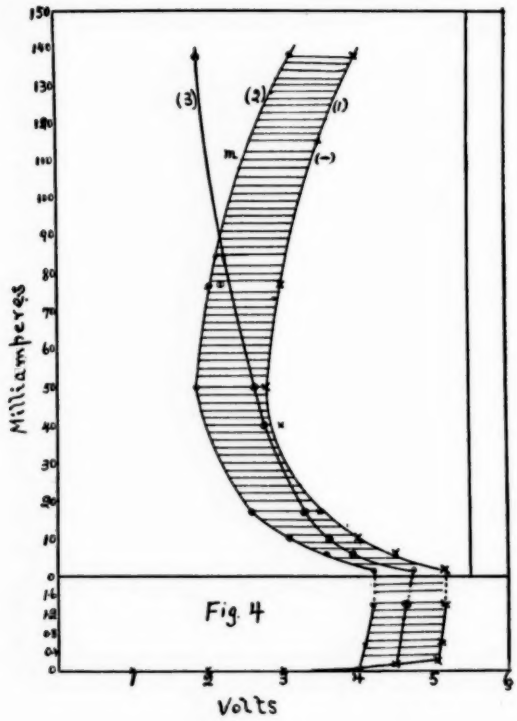



Fig. 4.

Some observations were made in a rapid stream of freshly distilled mercury vapor, close to the liquid surface, and Fig. 5 shows the current-voltage relation. Here we had two distinct breaks, one at 5.5 volts and another at 8.0 volts. The second break was evidently due to the setting in of ionization by single 10.4 volt impacts, the difference between 10.4 and 8 being just about that expected as a result of initial velocity distribution since the maintaining voltage, above the first break, was a little more than 2 volts below the theoretical 5.5 volts. On the return curve it is seen that, in addition to a break at 8 volts, the second arc is maintained to 6 volts. Consideration of relations such as curve (3), Fig. 4, shows that this second arc can reasonably be ascribed to single 10.4 volt impacts. The secondary 8 volt break was not observed with hotter filaments or higher vapor pressures. This is perhaps due to a dearth of

normal, unexcited mercury molecules in the immediate neighborhood of the filament when the arc current is very intense. We intend to investigate this point more fully.

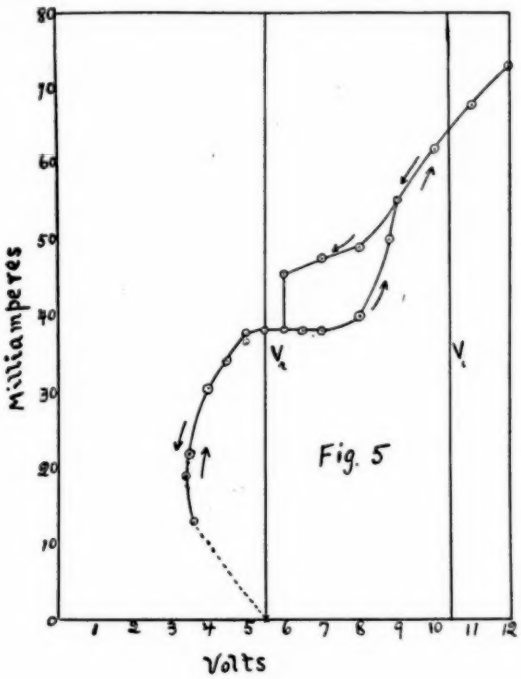



Fig. 5.

Attention may now be called to the fact that the theory developed in this paper can be applied to all gases and metallic vapors. For example, the difference between the ionizing potential and the radiation potential of sodium vapor is $5.13 - 2.1 = 3.0$, but Wood and Okano[1] observed that an arc could be made to strike at .5 volt, leaving 2.5 volts to be accounted for by the initial energy of emission. Compton, Lilly and Olmstead[2] found that the arc could strike in helium at 18.5 volts, while its radiation potential is 20.4 volts; an additional energy of 2 volts must, therefore, come from the initial velocities. In the case of mercury vapor Hebb[3] maintained an arc at 3.2 volts and we have maintained it at 1.8 volts, requiring on the average 3 volts to make up the minimum potential for cumulative ionization. In all three cases tungsten filaments were used, and the fact that the differences are of the same order of magnitude shows that they are characteristic of tungsten rather than that

[1] Wood and Okano, Phil. Mag., 34, p. 177, 1917.
[2] Loc. cit.
[3] Loc. cit.

of the gases used. Where platinum filaments have been used, the arcs have not been obtained at voltages much below the theoretical value. This is to be expected since platinum cannot be heated so hot nor can such a copious electron emission be obtained.

## Part II. Effect of Liquid Surface on Arcing Voltage.

### *First Apparatus.*

Having studied the phenomena with liquid mercury very close to the cathode, we proceeded to investigate them with the metal at various distances from it. The apparatus in its first form consisted of a straight tungsten filament (20 mil) with a coaxial cylindrical nickel anode, enclosed in a bulb made of G702P glass. There was a reservoir filled with mercury at a distance of 7 cm. from the cathode. To the main bulb was connected a coil of several turns of small glass tubing 180 cm. in length and 5 mm. in diameter. At the end of this long coil was provided a second reservoir with the mercury surface standing beside and at the same height as that in the first. Thence connection was made to the diffusion pump. The whole was heated by two electric heaters with the heating currents so adjusted as to keep the parts which contained no liquid mercury always at a temperature about 100 degrees higher than that of the reservoirs, the reason being to prevent any condensation from taking place in these regions.

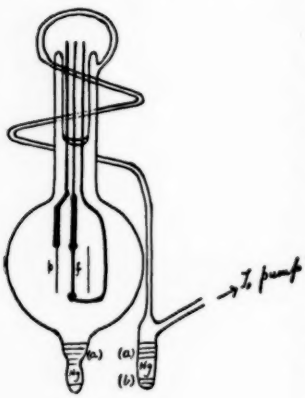


Fig. 6.

The electric connections and the necessary precautions preceding the experiments have been fully described in Part I. The procedure consisted in making observations with liquid mercury in both reservoirs, and then, other conditions being identical, repeating them with no liquid mercury in the main bulb. Owing, however, to the fact that we used large filament currents (from 28 to 34 amperes) with somewhat inadequate leads, and a long pumping system, it was very difficult to maintain a good vacuum for the length of time sufficient to enable us to take a continuous set of readings without impairing the filament. Accordingly, we set the applied voltage at a definite value and observed the striking of the arc by the indication of a sudden jump of the microammeter needle when the filament current was turned on. After one reading had been taken, the filament current was turned off to enable

any impurities (which were probably traces of water vapor from the glass near the leads) to be carried away by the pump. When the vacuum again became good, observation was made at some other definite applied voltage; and so forth. By adjusting the accelerating field by very small steps, we were able to determine the lowest striking voltage for a given vapor pressure and filament temperature under fairly good vacuum conditions.

### Results with First Apparatus.

Table II. shows the results obtained with this apparatus. The values given in (*a*) and (*b*) under the heading "striking voltage" were averages

Table II.

| Temperature of Reservoirs o° C. | Vapor Pressure in mm. | Striking Voltage (Mean) Measured to the Middle of Filament. | | Difference between (*a*) and (*b*) (Volts). |
|---|---|---|---|---|
| | | (*a*). | (*b*). | |
| 110 | .48 | 5.59 | 6.65 | 1.06 |
| 112 | .53 | 5.25 | 6.25 | 1.00 |
| 115 | .62 | 5.20 | 6.95 | 1.75 |
| 119 | .76 | —— | 6.90 | |
| 120 | .80 | —— | 6.52 | |
| 121 | .82 | —— | 6.45 | |
| 122 | .87 | —— | 6.85 | |
| 123 | .91 | 5.05 | 6.35 | 1.20 |
| 125 | 1.00 | —— | 6.86 | |
| 127 | 1.09 | 5.37 | 6.50 | 1.13 |
| 129 | 1.14 | —— | 6.55 | |
| 130 | 1.24 | 5.15 | 6.70 | 1.55 |
| 135 | 1.54 | —— | 6.40 | |
| 137 | 1.67 | 5.175 | —— | |
| 138 | 1.74 | 5.20 | 6.30 | 1.10 |
| 145 | 2.32 | 5.40 | 6.30 | 0.90 |
| | | | Mean | 1.21 |

(*a*) Distance between the liquid mercury and the cathode = 7 cm.; Filament current: 28–30 amperes.

(*b*) Distance between the liquid mercury and the cathode = 180 cm.; Filament current: 30–34 amperes.

of four or five readings for each temperature. Thus, out of more than 60 readings with vapor pressures ranging from .48 to 2.32 mm., we found no single instance of the effect of 4.9 volts in the case (*b*), which differed from (*a*) only in the distance between the liquid mercury and the cathode. In case (*b*) it was found impossible to produce the arc at low voltages without using a somewhat hotter filament than in case (*a*), as indicated below the table. This change favors the production of the low voltage arc, so that we may say that the 4.9 volt arc did not occur in

case (*b*) in spite of more favorable conditions as regards filament temperature. The values in both cases represent definite minimum arcing voltages which could not be diminished by further increase in the filament temperature except by the relatively small amount due to increased initial velocity of emission. It is true that the values of minimum striking voltage in (*a*) and (*b*) do not represent the true values; they merely set the lower limits beyond which the true values cannot go. For the true values are obtained by adding to these values the mean initial energy and a small fraction of half the potential drop in the filament, depending on the point of the filament to which the arc strikes. These corrections are, however, small in comparison with the difference between the values in the two cases, and are approximately the same for both cases. Thus the difference between the two cases is a real one, and is significant.

The mean difference between the two cases (1.21 volts) is almost exactly equal to the difference (6.7 − 5.5 = 1.2 volts) which we would expect if the 4.9 volt effect, due to λ 2536 resonance radiation, determines the minimum arcing voltage in mercury vapor near the liquid surface while the 6.7 volt effect, due to λ 1849 resonance radiation, determines the arcing voltage in vapor far removed from the liquid. In any case, we are led to believe that the arcs in these two cases are produced by mercury molecules which are in different conditions.

### *Second Apparatus.*

With a view to confirming the preceding results and throwing some new light upon the problem, the following apparatus was adopted.

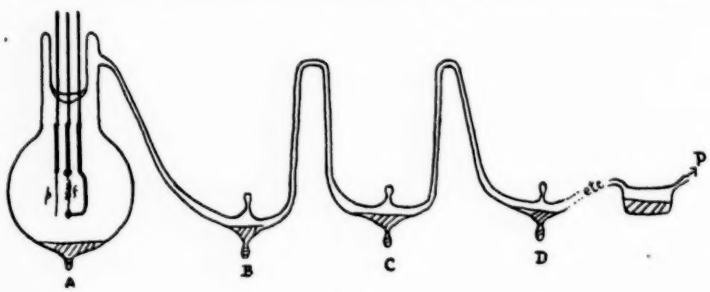



Fig. 7.

Distance of filament *f* from reservoir: *A* = 5 cm., *B* = 35 cm., *C* = 70 cm., *D* = 107 cm.

A coiled tungsten filament of five turns with a nickel anode plate was enclosed in the main bulb *A*, whence connection to the pump was made through a small glass tube of 310 cm. in length. In its course at

intervals specified below the diagram, were provided small reservoirs of such design as to make easy the process of filling in and drawing out the liquid mercury. The one nearest the pump was the largest among them. Before the whole was immersed in a paraffin oil bath, the mercury in all the reservoirs was thoroughly boiled. When the whole apparatus was immersed in the hot paraffin oil, to secure the desired vapor pressure, an attempt was made to arrange the heating burners so as to produce a slight temperature gradient to prevent the condensation of mercury in any part of the system nearer to the electrodes than the nearest reservoir containing mercury. This was successful in every case except Case *B*, described below. The procedure consisted in taking in turn readings with mercury in the reservoirs *A*, *B*, *C*, and *D*; *B*, *C*, and *D*; etc. Great care was taken to clean mercury from the path leading from the electrodes to the nearest filled reservoir, while keeping the succeeding reservoirs full of mercury. The reason for keeping succeeding reservoirs full was to prevent any rapid stream of mercury vapor from passing over from the experimental reservoir, thus insuring approximately an equilibrium condition and a vapor pressure really characteristic of the temperature. The difficulty mentioned above, of getting a good vacuum after the filament current was turned on, was minimized by using a tungsten filament of lesser size and with larger leads.

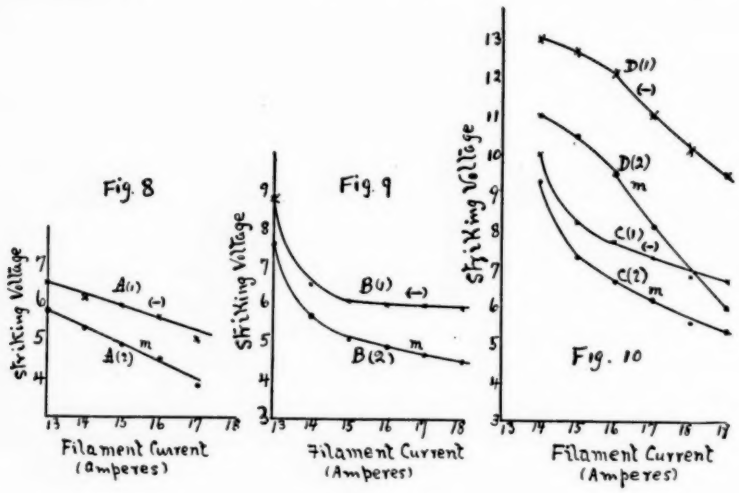
### *Results with Second Apparatus.*

Since we had found the effect of the liquid surface within a wide range of vapor pressures, we confined ourselves now to the study of the relation between the filament current and the striking voltage at some suitable vapor pressures. The results were as follows.

*Case A.*—The distance between the liquid mercury in the reservoir *A* and the cathode was 5 cm. Here no trace of the effect of 6.7 volts was found; all effects were due to that of 4.9 volts. The relation between the filament current and the striking voltage was linear, in conformity with our previous results in Part I.. See Fig. 8. $A(1)$ is measured to the negative end and $A(2)$ to the middle of the filament. The difference between the observed voltages and 5.5 volts is accounted for by initial velocity of emission, as shown in Part I.

*Case B.*—The distance between the liquid mercury in the reservoir *B* and the cathode was 35 cm. Here the values of the striking voltage at higher filament temperatures were only slightly higher than those in Case *A*. The 4.9 volt arc was still prominent. After the readings had been taken, it was found, however, that a trace of liquid mercury had been left by mistake in the reservoir *A* and condensation had taken

place along the tube leading from the reservoir $B$ to the cathode, indicating that there had been a stream of mercury vapor in toward the electrodes. The significance of this case will be discussed later. See Fig. 9.




Figs. 8, 9, 10.

*Case C.*—The distance was increased to 70 cm. If we compare the curves $C(1)$ and $C(2)$ in Fig. 10 with $A(1)$ and $A(2)$ in Fig. 8, we see that there was on the average a difference of 2.0 volts in the values of the striking voltage. Since in Case $A$ we have positively identified the effect of 4.9 volts, the production of arcs in Case $C$ must be due to that of a higher critical voltage, presumably 6.7 volts.

*Case D.*—A new tube leading from the main bulb to the reservoir $D$ was used, with a distance between the liquid mercury and the cathode equal to 107 cm. The position of the main bulb was so tilted that no liquid mercury could possibly enter or stay in it. At the end of Case $C$, the filament was burned out and a new one was put in. Unfortunately, it was a little too long, and in consequence the potential drop across it was rather large, which rendered the true values of the striking voltage a little uncertain. But even in this case the experimental curves did set the limits within which the true value at the highest temperature should lie. The vacuum conditions in this case were particularly satisfactory. See Curves $D(1)$ and $D(2)$ in Fig. 10.

In all these cases it has been brought out unmistakably that the striking voltages, corrected for initial energy of electrons, all tend toward definite minimum values as the highest filament temperature was approached. This is especially evident when it is remembered that the arcing voltage,

corrected for filament drop, lies between curves (1) and (2), Fig. 3, in all these cases, and is nearer curve (2) at lower temperatures and curve (1) at the highest temperatures. When the liquid mercury was very near the cathode, the limiting value was in the neighborhood of 5 volts. When it was far removed, this was never below 6 volts. Another very noticeable fact, which strengthens the belief that we are really dealing with two different types of arc, is that, when near the liquid surface, the arc not only struck at a lower voltage but would strike much more easily, *i.e.*, with lower filament temperatures and much less care regarding good vacuum conditions, than when the liquid surface was remote.

The contrast between these two cases finds its expression also in the curves in Figs. 11 and 12. The changes between the striking and breaking voltages were reversible in both cases; but in one the arc struck and broke at 6.2 volts with less filament current and in the other at 7.5 volts with larger filament current. Voltages are given to the negative end of the filament in both cases.

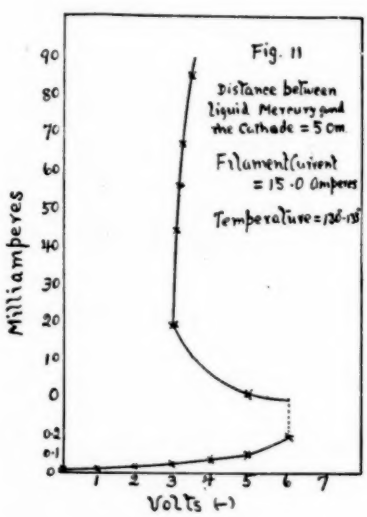



Fig. 11.

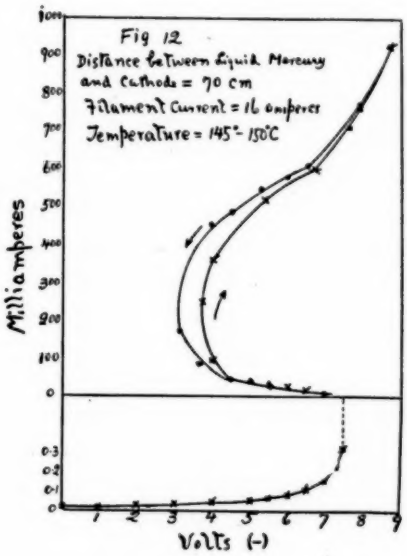



Fig. 12.

*Third Apparatus.*

If there is still any doubt about the existence of two types of arc, the following experiments will help to remove it. The apparatus was designed to permit the attainment of the highest possible purity of mercury vapor and greater flexibility in methods of testing. The first end was attained by constructing the apparatus so that it formed of itself a diffusion pumping system in which any impurities evolved in the region of

the electrodes were automatically carried away toward the vacuum pump by the motion of the mercury vapor. This is evident from the construction shown in Fig. 13.

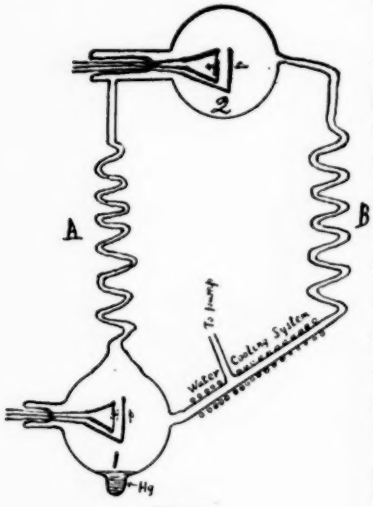



Fig. 13.

Two bulbs with identical electrodes were connected by two equal pieces of glass tubing, so as to form a closed circuit. A water cooling jacket was provided near the connection to the pump, as shown. The whole was enclosed in an electrically heated asbestos oven so arranged as to maintain a small upward temperature gradient, thus preventing any condensation of mercury in the tubes *A* or *B* or in bulb (2). Before making observations the mercury was thoroughly boiled, the glass parts well baked out and the electrodes thoroughly glowed, a high vacuum being maintained by a two-stage diffusion pump.

Observations of the striking and maintaining voltages of the arc were made with various filament currents in the following four conditions: (*a*) in bulb (1) in stagnant vapor (with the water-cooling system not in operation); (*b*) in bulb (2) in stagnant vapor; (*c*) in bulb (1) in moving vapor (with the water-cooling system in operation); (*d*) in bulb (2) in moving vapor. In cases (*a*) and (*b*) the vapor pressure was the same. In case (*d*) the vapor pressure would be about half that in case (*c*) owing to the fall in pressure along the tube of moving vapor. This was compensated very nearly by using a slightly higher temperature of the mercury reservoir in case (*d*) than in case (*c*). Thus any difference between the results in cases (*c*) and (*d*) cannot be attributed to difference in vapor pressure, since the earlier experiments showed that the striking voltage was practically constant over a considerable range of pressures. These four cases were tried with tubes *A* and *B* of 100 cm. length and 5 mm. diameter, and again with tubes of 50 cm. length and 1 cm. diameter. Experiments were tried at various temperatures of the mercury reservoir between 130° and 150° C.

### *Results with Third Apparatus.*

The results entirely confirmed those with the first two types of apparatus. Table III. is an example, taken with tubes *A* and *B* of 100 cm. length and stagnant vapor, cases (1) and (2).

TABLE III.

| Filament Current (Amperes). | Striking Voltage to Negative End of Filament. | | Difference between (*a*) and (*b*) (Volts). | Maintaining Voltage to Negative End of Filament. | | Difference between (*a*) and (*b*). |
|---|---|---|---|---|---|---|
| | (*a*). | (*b*). | | (*a*). | (*b*). | |
| 13..... | 7.2 | 8.55 | 1.35 | 5.1 | 5.8 | 0.7 |
| 14..... | 6.7 | 7.90 | 1.20 | 3.8 | 4.3 | 0.5 |
| 15..... | 6.1 | 7.77 | 1.67 | 3.2 | 3.85 | 0.75 |
| 16..... | 5.9 | 7.20 | 1.30 | 3.1 | 3.67 | 0.57 |
| 17..... | 5.7 | 7.00 | 1.30 | 3.0 | 3.57 | 0.57 |
| 18..... | 5.5 | 6.70 | 1.20 | 3.0 | 3.3 | 0.30 |
| | | | Mean = 1.33 | | | Mean = 0.56 |

The average difference between the striking voltages in the two cases was 1.33 volts, agreeing well with the suggested theoretical difference of 1.2 volts. The difference between the maintaining voltages was less, and is probably not significant.

Results practically identical with those above were obtained in the moving vapor in tubes *A* and *B* of 100 cm. length and in stagnant vapor with tubes of 50 cm. length. In moving vapor with tubes of 50 cm. length a small liquid surface effect was shown in the current-voltage curve of bulb (2). This suggests that the apparatus may be modified to permit measurement of the life period of the abnormal mercury molecules which originate at the surface of evaporation. Such an investigation can not be included in the present paper.

## DISCUSSION.

The question arises as to whether the difference between the values of the striking voltage in these two cases may not be attributed to impurities. For, one argues, if mercury vapor diffuses from the bulb containing the electrodes, this vapor will carry out any impurities which may be given off in the bulb, and thus create a better vacuum in case the liquid is placed under and very near the cathode. On the other hand, if the liquid is far away, these foreign gases would hinder the production of a good vacuum in the arcing space, and, therefore, a higher potential would be required in order to produce the arc. We have direct experimental evidence to show that this objection is unfounded. In the first place, the distribution of mercury reservoirs was such as to preclude any considerable motion of mercury vapor in the first two types of apparatus, as previously pointed out. In the second place, we found by experience that, with mercury very close to the cathode, it was exceedingly easy to

get the 4.9 volt arcs at low voltages, even when the vacuum was not very good. But, if the liquid surface was far away, a slightest trace of impurities rendered the production of the 6.7 volt arc difficult, and the 4.9 volt arc was never obtained. In the third place, we have the Case *B* with the second apparatus where the indication was such as to show that the direction of the stream of mercury vapor was from the distant reservoir *into* the arcing space, and if there were any impurities they must drift along that direction and tend to be retained in the bulb. Yet the 4.9 volt arc appeared just the same. This fact alone suffices to remove the objection quite apart from the numerical agreement with the theoretical values. Finally, in the third apparatus, conditions for removal of impurities were ideal.

Another suggested criticism is that, if we were working with mercury molecules in an abnormal state, the liquid surface ought to have no influence as soon as *equilibrium* has been established. But it must be remembered that the molecule of a freshly distilled vapor remains in its abnormal state only for a short interval, during which it is more capable of absorption of radiation, which in turn renders it easily ionized by direct electronic impacts. This condition is fulfilled when the liquid surface and the filament are very close to each other. If they are far apart, then by the time it reaches the arcing space the molecule has already returned to its normal state, or to a state in which it will not so readily (if at all) absorb the resonance radiation λ 2536; hence a higher potential must be applied, probably high enough to stimulate the λ 1849 radiation. The question whether, or to what relative extent, λ2536 will be absorbed by the vapor in a tube containing no liquid mercury is important, and should be investigated, as has been pointed out by Professor Wood.[1]

Closely related may be the work of McLennan and Shaver,[2] who have found that, by the photographic method as well as by the use of thalofide cells, non-luminous mercury vapor does not absorb radiation of the wave-length λ 10140. But if there are scarcely visible deposits of mercury in the tube it shows marked absorption of this radiation. This may account for the absorption of λ 10140 by non-luminous vapor observed by Dearle.[3] It would be interesting to study the absorption by a long column of mercury vapor with the exciting light parallel to and grazing the liquid surface as compared with the absorption at some distance from the mercury surface, as Professor Compton once suggested.

Whatever may be the interpretation, it is now experimentally proved

[1] Loc. cit.

[2] McLennan and Shaver, Proc. Roy. Soc., 100, p. 200, 1921.

[3] Dearle, Roy. Soc. Proc., *A*, 92, p. 608, 1916; 95, p. 280, 1919.

that there is a close relation between the production of arcs on the one hand and the excitation of fluorescence and resonance radiation on the other, in mercury vapor. These experiments also open the question as to the origin of the spectral lines λ 2536 and λ 1849. According to the Quantum Theory, the resonance potential of 4.9 volts corresponds to the first term of the combination triplet series $1S - mp_2$ and that of 6.7 volts to the first line of the principal singlet series $1S - mP$. And according to the Bohr theory it means that the line λ 2536 is emitted when the electron falls from the $1p_2$ orbit to the $1S$ orbit, and when it falls from $1P$ to $1S$ the line λ 1849 is emitted. In the light of our experiments these lines seem to originate from different entities. The suggestion,[1] that diatomic molecules may come out from a freshly distilled vapor and account for the fluorescence is, apart from lack of chemical evidence, not supported by the positive ray spectrum of mercury, nor is it in accord with Bohr's theory of radiation. These experiments, therefore, suggest more problems than they attempt to solve, and it is to be hoped that further investigation along these lines may throw some light on the problems. For the fact that λ 2536 and λ 1849 belong to series having identical convergence limits and the fact that there is only one ionization potential, 10.4 volts, makes it very unlikely that there are really two different entities. The most plausible explanation in the light of present knowledge seems to be that there is some slight influence either due to arrangement of internal electrons or to influence of neighboring molecules which increases the probability of ionization along the $1S - mp_2$ path as compared with the $1S - mP$ path in freshly distilled vapor, but that this influence does not appreciably affect the potential energy of the electron in the $1S$ state. In other words, the direction or size of the force on the electron may differ while the energy does not. This is, of course, dynamically possible.

In conclusion, I wish to express my sincere thanks to Professor K. T. Compton, who suggested this research and under whose direction it was carried out.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
August 14, 1922.

[1] J. S. Van der Lingen and R. W. Wood loc. cit.

# HALL EFFECT AND SPECIFIC RESISTANCE OF EVAPORATED FILMS OF SILVER, COPPER AND IRON.

By J. C. Steinberg.

Abstract.

**Specific resistance and Hall coefficient of evaporated films, 20 to 200 $\mu\mu$ thick.**—The specific resistances of films of *silver, copper and iron* were found to be from 15 to 57 times the values for the bulk metals, being respectively 24.3, 29.7 and 506 instead of 1.6, 1.8 and 8.8. The Hall coefficients of films of silver and copper, two diamagnetic metals, were respectively 41 and 11 per cent. *less* than the bulk values, while for the iron films the coefficient was + 42.5 as compared with + 6.6 for bulk iron, an *increase* of over 500 per cent. For the silver and copper films the Hall effect is proportional to the field throughout, but for iron films the proportionality extends only to 10,000 gausses, whereas the limit for bulk iron is 20,000 gausses. This indicates that the *maximum intensity of magnetization in iron films* is only half as great as that attainable in pure bulk iron.

**Structure of evaporated metal films.**—X-ray analysis showed that films of silver and iron and probably other metals have the same crystal structure as the bulk metals, but the crystal grains are too fine to distinguish with a microscope.

**Effect of extreme fineness of crystal structure on certain physical properties of metals.**—The increase of *specific resistance* is probably due to the multiplication of the number of contacts between grains. The *Hall coefficient* is practically independent of the structure except as it affects the magnetic condition of the crystals. The *intensity of magnetization* in iron crystals seems to be limited by the demagnetizing action of the poles of the crystals, which is greater the smaller the crystal grains.

**Method of producing uniform metallic films by evaporation.**—This involves moving a heated filament uniformly over the surface to be coated, at a distance less than the mean free path in a high vacuum. The films are hard and bright and resist corrosion.

## Introduction.

THIS work extends an investigation on chemically deposited silver films by G. R. Wait[1] to films obtained by evaporation. For a discussion of the various film phenomena, and references of historical interest, the reader is referred to Wait's publication. Wait concludes that his results as well as the results of others are consistent with the conception that the film consists of granules, each granule having the properties of the bulk metal.

Evaporated films were employed in order to learn more of the nature of these granules. The Hall effect and the specific resistance were measured in films whose thicknesses varied from 20 to 200 $\mu\mu$. The

[1] G. R. Wait, "Hall Effect and Specific Resistance of Silver Films," Phys. Rev., 19, 615, 1922.

films were examined under a microscope for traces of structure, and also subjected to x-ray analysis.

## Experimental Method.

The essential features of the evaporation method of obtaining a film consist in drawing an electrically heated filament of the metal back and forth over a microscope slide in vacuum. Both glass and quartz slides were used. The particles of metal given off by the hot filament adhere to the microscope slide, giving a uniform film.

The details of the evaporation apparatus are shown in Fig. 1. Two

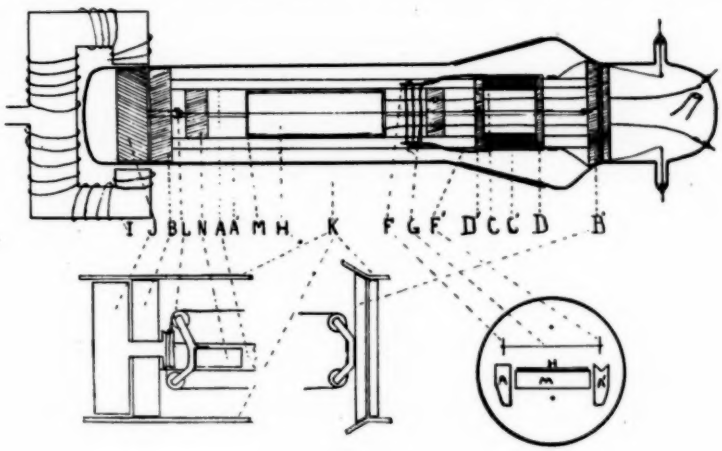



Fig. 1.

brass tracks $AA'$ are fitted into the cylindrical fibre plugs $BB'$. Ground to fit the tracks are two brass blocks $CC'$, which, held rigid by the fibre straps $DD'$, constitute the carriage. The mica strips $FF'$ serve to support the wire $G$ connected across the blocks. The electro-magnet $I$ turns around the pyrex tube $K$. Inside the tube, the iron core $J$ turns with the magnet. By means of a small capstan $L$, the carriage is drawn along the tracks. The electro-magnet, which was designed by Dr. G. R. Wait and Mr. J. B. Dempster, is so constructed that it reverses its direction of rotation every three revolutions, and turns with constant angular velocity. Thus the carriage moves uniformly back and forth along the tracks. $M$ is a small heating element to drive occluded vapors from the microscope slide $H$, prior to evaporation. Current is furnished the wire by means of leads connected to the brass tracks.

The tube was connected to a Knipp mercury vapor pump, with a Gaede mercury pump and a water aspirator as fore-pumps. The pumps which were very rapid were kept in operation during evaporation. Pre-

cautions were taken to insure the pressure being reduced to such a value that the maximum distance of the wire from the glass slide would be less than the mean free path of the gas molecules. The required pressure was .001 mm. mercury. As a rough indication, the pressure was reduced sufficiently to enable a spark to jump a one and one half inch air gap in parallel with the electrodes of an attached discharge tube.

It was found necessary to give a new wire a preliminary evaporation before desirable films could be obtained. In practice the wire was maintained at its evaporation temperature several hours before taking a film. When this precaution was not observed, the films obtained were found to be erratic in behavior and not constant with time. Etching the wire prior to evaporation did not eliminate the effect to any marked extent. Metals of very good purity were used, and the evaporated metals were probably very pure.

For microscopic examination a Bausch and Lomb metallurgical microscope was employed. X-ray analysis was made by means of a method described by Hull.[1] The apparatus used for the work was kindly loaned by Dr. C. W. Hewlett, and a description of its method of operation may be found in his publication.[2] The metals were evaporated under the same conditions as the films, and scraped from the surfaces upon which they were deposited. They were then finely powdered, and suitably mounted in a homogeneous beam of x-rays from a molybdenum target. A filter of zirconium powder .037 cm. thick reduced the spectrum to approximately a single line, of wave-length .712 A.U. The angular deviations of the lines were determined by observing the rate of discharge of an ionization chamber.

Hall effect and specific resistance were measured in a manner similar to that described by Wait.[3] Thickness was determined by weighing, assuming the density to be that of the bulk metal. This assumption is justified on the grounds that any sensible change in density would not account quantitatively for the magnitude of the observed effects.

## Results.

The Hall effect in a film is given by the relation,

$$E = \frac{RHI}{\epsilon},$$

where $E$ is the Hall e.m.f., $R$, the Hall coefficient, $H$ the magnetic field, $I$ the current through the film, and $\epsilon$ the thickness of the film. $E$, $H$, $I$,

[1] Phys. Rev., 10, p. 661, 1917.
[2] C. W. Hewlett, Phys. Rev., 20, 688, 1922.
[3] Wait, loc. cit.

and $\epsilon$ are determined experimentally and $R$ computed. The values given in Table I. were obtained during the investigation when not otherwise indicated.

TABLE I.

| Metal. | $R \times 10^5$ (e.m.u.). | $\rho \times 10^{-3}$ (e.m.u.). |
|---|---|---|
| Taken from | | |
| Bulk Silver (pure)—Smithsonian Tables | −88.0 | 1.6 |
| Chem. Dep. Silver | −86.4 | 2.7 |
| Evaporated Silver | −52.0 | 24 3 |
| Bulk Copper (pure)—Smithsonian Tables | −56.0 | 1.8 |
| Evaporated Copper | −50.0 | 29.7 |
| Bulk Iron (pure)—A. W. Smith[1] | + 660 | 8.8 |
| Evaporated Iron | +4250 | 506.4 |

*Evaporated Silver Films.*

The Hall coefficient in evaporated silver is negative and independent of the thickness. The value given in Table I. is the average of the values obtained from a large number of films whose thicknesses varied from 20 to 200 $\mu\mu$. In Fig. 2, experimental values of $E/HI$ are plotted against $\epsilon$. The curve drawn through the points is a graph of the equation $E/HI = R/\epsilon$, where $R$ has the average value obtained from the films.

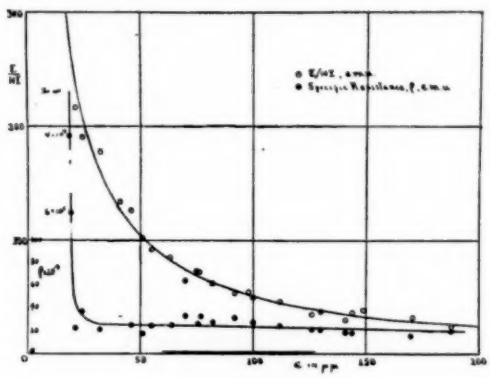


Fig. 2.

The specific resistance $\rho$ as a function of thickness is also shown in Fig. 2. Its behavior is similar to that found in films obtained by other methods. The average value, taken from films whose thicknesses are greater than the critical thickness, *i.e.*, the thickness at which $\rho$ becomes infinite, is given in Table I. It is to be noted that we have here a large increase in $\rho$ as compared with bulk silver, about 1,000 per cent., and a relatively small change in the Hall coefficient. The straight line in

[1] PHYS. REV., 30, p. 1, 1910.

Fig. 2, near the axis of abscissas, indicates the value of $\rho$ for bulk silver. The resistances of the films remained sensibly constant with time.

The x-ray analysis was only qualitative, it being desired merely to determine whether or not the metal was crystalline. From data published by Hull,[1] the angular deviations of the most intense lines were computed, and found to coincide within the error of the experiment, to the lines observed with evaporated silver. The existence of the lines in their computed positions was taken as sufficient evidence that the metal was crystalline, and of the type found in bulk silver, that is, with the face-centered cubic lattice, of elementary side 4.06 A.U.

The films obtained were hard and very uniform in thickness. They possessed an excellent reflecting surface, and did not deteriorate readily with age. Repeated attempts to observe granular structure under a microscope failed. The films appeared blue by transmitted light, which is the characteristic color of silver.

*Evaporated Copper Films.*

Evaporated copper was found to behave in a manner similar to that of evaporated silver. The average values of $R$ and $\rho$ are given in Table I. The values of $E/HI$ against $\epsilon$, and $\rho$ against $\epsilon$, are plotted in Fig. 3. As in the the case of silver, evaporated copper has a large specific resist-

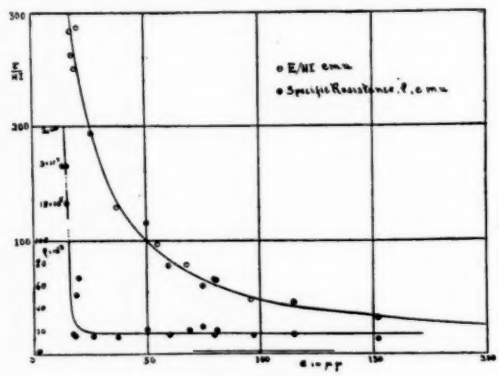


Fig. 3.

ance, although the Hall coefficient does not differ appreciably from the bulk value.

The copper films like silver were very good reflectors, although they reflect slightly more to the red than does silver. They appear green by transmitted light. Structure analysis was not made for the copper films.

[1] Hull, loc. cit.

*Evaporated Iron Films.*

Evaporated iron films behave in a manner similar to bulk iron in that they have a positive Hall coefficient which is not constant with magnetic field. Fig. 4 shows the relation between the Hall e.m.f. and the magnetic field for several films of different thicknesses. It will be seen that $E$ is proportional to $H$ up to fields of about 10,000 gausses. For bulk iron this proportionality holds for fields up to about 20,000 gausses. The bend in the curves is spoken of as the saturation of the Hall e.m.f. The average value of the Hall coefficient given in Table I., is computed for fields below 10,000 gausses by means of the relation

$$E = \frac{RHI}{\epsilon}.$$

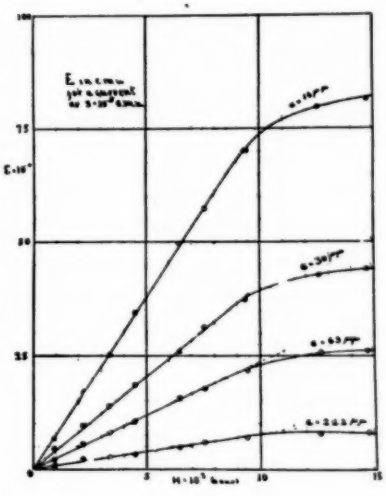


Fig. 4.

In contrast to its behavior in copper and silver, the Hall coefficient of evaporated iron shows an increase of about 600 per cent. over that of the bulk metal.

Wire containing 99.85 per cent. iron was used, so that the films obtained were relatively pure. The films appeared silver white by reflected light, and rather brownish by transmitted light. No trace of structure was visible under the microscope. The films reflect very well, were hard, and did not oxidize readily in air.

Evaporated iron was found to be crystalline, the lines occurring at the angular deviations computed from Hull's data.[1] As in the case of silver, it is inferred from the correspondence of these lines that the type of lattice is that found by Hull, which in iron is the centered cubic, of elementary side 2.86 A.U.

DISCUSSION.

Let us consider in more detail the nature of evaporation in the sense that we use it. The wires were run at temperatures[2] that correspond to a vapor pressure of $10^{-3}$ mm. of mercury. At this pressure, the distance of the wire from the microscope slide was less than the mean free path. It has been found that metallic vapors are monatomic.[3] Then if the

[1] Hull, loc. cit.

[2] Johnston, Journ. Ind. Eng. Chem., 9, p. 873, 1917.

[3] Meyer, Ber., 12, p. 1426, 1879.

atoms are not reflected [1] upon striking the slide, the film must be deposited an atom at a time, the atoms reaching the slide without collision with each other. Since the evaporated metals are crystalline, some of the atoms evidently do not take random positions, but take definite places in a lattice, probably under the influence of the atoms already there. It is thought that rapid evaporation with a large temperature difference between the slide and the wire would tend to diminish crystalline growth.

The term crystalline grain is used in the sense employed in metallurgy,[2] that is, to designate a crystal of metal, in which the elementary crystals all have the same orientation. Its properties are supposed independent of the manner of obtaining it, as long as the same type of elementary crystal is obtained. Any specimen of metal is, in general, made up of an aggregate of crystalline grains separated by boundaries. The properties of the specimen are supposed to depend upon the size of the crystalline grains, and upon the contacts between them.

We conclude that in evaporated films, the crystalline grains are much smaller than in bulk metals, and that they are not in the intimate contact obtaining in bulk form. This view is supported by the fact that the metals have been found to be crystalline, that the crystalline grains were not visible under a microscope, that the surfaces of the films appear to have a very high polish, and that the essential nature of the process of obtaining them is not conducive to crystalline growth.

The large resistivity of evaporated metals leads us to believe that the resistivity of a specimen of metal will be smallest at a given temperature and pressure, when the specimen is a pure metallic crystal. The effect of the boundaries that separate adjacent crystalline grains is to increase the resistivity of the specimen. This increase is very pronounced when impurities are present that freeze out in the process of solidification. An idea of the effect upon the resistivity of a change in the size of the crystalline grains alone can be obtained by comparing the resistivity of two specimens of pure metal, the one obtained by sudden quenching, the other by slow cooling, during solidification.

The results on silver and copper indicate that the Hall coefficients of these substances do not change appreciably when the structure is changed. This might be expected, since the supposition that the impressed magnetic field produces the transverse e.m.f. accounts well for the observed effects. In the case of iron, however, for which the Hall coefficient is positive and therefore intimately associated with the molecular fields, one might expect structure to have a pronounced influence.

[1] Langmuir, PHYS. REV., 8, p. 149, 1916.

[2] See Sauveur, "The Metallography of Iron and Steel," and Rosenhain, "The Study of Physical Metallurgy."

A. W. Smith[1] has found that as temperature is increased, the Hall coefficient of iron increases, and the value of the magnetic field at which the Hall e.m.f. becomes saturated shifts to smaller fields. He points out that the saturation of the Hall e.m.f. should occur when $H = 4\pi I_m'$, where $I_m'$ is the maximum value of the intensity of magnetization, and that the decrease of $I_m'$ as temperature is increased accounts for the observed shifts. Now our proportionality between $E$ and $H$ holds only up to one half the value of $H$ for pure bulk iron. Furthermore the directional change in $R$ is the same in the two cases. Thus it appears that if the Hall effect is essentially the same phenomenon in the two cases, $I_m'$ for evaporated iron is less than that for bulk iron.

The results indicate, then, that the effect of decreasing the size of the crystalline grains has been to decrease the maximum value of the intensity of magnetization that can be attained in the iron. This is not so surprising if we suppose that the permeability of the boundaries is different from that of the crystalline grains. Then each crystalline grain would have poles at the boundaries, and as the grains become smaller, the poles would exert a greater demagnetizing force. It does not seem improbable that a perfect crystal of iron would have the greatest $I_m'$, and that the difference between $I_m'$ for a perfect crystal and for a specimen of like size and shape, but made up of crystalline grains, would be a measure of the demagnetizing effect of the poles. Thus it appears that new importance is attached to the experiments in that they bear upon the nature of ferromagnetism.

In conclusion, I wish to express my appreciation to the members of the Department of Physics of the State University of Iowa for their assistance and interest, and especially to Dr. G. W. Stewart, under whose direction the work was carried on.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
August 20, 1922.

[1] PHYS. REV., 30, p. 1, 1910.

# X-RAY ABSORPTION COEFFICIENTS OF CARBON, HYDROGEN AND OXYGEN.

By A. R. Olson,[1] Elmer Dershem, and H. H. Storch.

Abstract.

**Absorption coefficients of water and six organic liquids for x-rays of wave-lengths 0.2 to 0.98 A.**—A large accurate spectrometer was used to disperse the rays from a Coolidge tube, whose current and voltage were kept constant within 0.1 per cent., and the beam entering the ionization chamber was so narrow that the range of wave-length included was only from 1.7 to 3 per cent. of the mean. The absorption cells, either 1 cm. or 10 cm. deep, were placed 10 cm. in front of the ionization chamber; therefore the absorption measured includes scattering. The variation with wave-length, at least between 0.35 and 0.98 Å., was found in all cases to be in accordance with the equation $\mu = A + B\lambda^3$, where for *water, benzene, toluene, xylene, mesitylene, heptane and cyclohexanol* the values for $A$ are 3.5, 15.3, 19.0, 21.7, 24.2, 21.5 and 20.5, respectively, and those for $B$ are 44.5, 74.9, 85.3, 98.3, 113.6, 87.3 and 121.0, respectively. These values give the coefficients for a gram molecule of each liquid in a cell 1 cm.$^2$ in cross section.

**Mass absorption coefficients of hydrogen, carbon and oxygen for x-rays of wave-lengths from 0.25 A. to 0.98 A.,** computed from the above measurements, are as follows: $\mu_H = 0.37 + 0.28\lambda^3$, $\mu_C = 0.18 + 1.01\lambda^3$, $\mu_O = 0.16 + 2.785\lambda^3$. The remarkable agreement between these values for carbon and oxygen, and Hewlett's values for graphitic carbon and liquid oxygen prove the validity of the additive law. The curve for hydrogen suggests that the absorption of this element does not follow the cube law for wave-lengths shorter than 0.65 Å., but is nearly constant down to 0.4 Å.

AUREN,[2] using non-homogeneous x-rays, found a large discrepancy between the absorption coefficients of graphite and carbon in organic combination. If this difference were real, aliphatic and aromatic carbon should likewise differ from each other because of the difference in their bonding. We therefore have repeated some of Auren's work, confining our attention to compounds of carbon, hydrogen and oxygen, taking advantage of the refinements that have been made in x-ray apparatus since the former work was done.

## Description of Apparatus.

The ordinary type of Coolidge x-ray tube with tungsten target was used in this work. The current through the tube was measured by a specially constructed galvanometer and could be maintained constant to within less than 0.1 per cent. by regulating the heating current of the tube

[1] National Research Fellow in Chemistry.

[2] Auren, Phil. Mag., *37*, 165 (1919).

filament. This was done by means of a rheostat constructed of iron wires which could be lowered into or raised out of tubes filled with mercury, thus making it possible to vary the heating current by very small amounts, and at the same time secure perfect electrical contact throughout the circuit.

To secure a constant potential for the x-ray tube, a direct-connected motor-generator set was used, the direct-current motor being driven by storage batteries and the alternating-current generator supplying the primary of the x-ray transformer. With this arrangement the potential could be maintained constant to within 0.1 per cent.

The spectrometer was a large and finely made instrument with an eleven-inch circle which could be read with the aid of microscopes to 1″ of arc had such precision been desired in this work. The front slit was 28 cm. from the crystal, and just in front of the latter, as close as possible to it, another slit was placed. The ionization chamber slit was likewise 28 cm. from the crystal, thus keeping it on the focal circle with respect to the forward slit. The ionization chamber was 44 cm. long, and was filled with methyl iodide vapor. Others find great difficulty in the use of this gas owing to its activity in attacking all kinds of insulation, but we found that if it were purified and dried, phosphorus pentoxide being kept in the ionization chamber, the insulation would remain perfect over several months' time. A string electrometer having a sensitivity of about 50 divisions per volt was attached to the ionization chamber. The combined electrostatic capacity of ionization chamber and electrometer was about 13 cm.

The cells used to contain the liquids were made by drilling holes 1.9 cm. in diameter through plate glass of about 1 cm. thickness. Microscope cover glasses were then cemented over these holes with water glass, thus making tubes of accurately known length for containing the liquids. For the shorter wave-lengths glass tubes 10 cm. long, the ends of which were closed by microscope cover glasses, were used. These cells were placed about 10 cm. in front of the ionization chamber, and hence practically none of the radiation scattered in the cell could enter the narrow slit of the ionization chamber. Under these conditions the absorption coefficients measured included both the scattering and fluorescent absorption.

The time intervals were measured by means of an electromagnetically operated counter which recorded the number of beats of an electrically driven tuning fork beating fifteen times per second. This was found much more accurate and satisfactory than a stop-watch, especially for short time intervals.

The zero position of the ionization chamber was found by measuring the absorption coefficient of a thin piece of silver for wave-lengths near that of the $K$ absorption limit for silver. The absorption coefficients were then plotted against ionization chamber angles. This gives a sloping line, the center of which indicates the position of the chamber for a mean wave-length of 0.483 Ångstrom unit, and the extremities of this sloping line give the range of chamber angles over which waves of this length may enter the chamber and hence may be used to determine the extreme variation of wave-length in the beam entering the chamber. Calibration curves made in this way show that in this work the extreme variation in wave-length from the mean value used in the calculations amounted to 1.5 per cent. for the smallest angles and 0.85 per cent. in the case of the largest angles.

The method of taking observations is too well known to require exposition in this article. To facilitate calculation, our results are converted into gram mol absorption coefficients, *i.e.*, the absorption coefficient of a column of liquid one cm. in cross section, and of such a length as to contain one gram mol. These data are given in Table I. and plotted in Figs. 1 and 2 as functions of the cube of the wave-length.

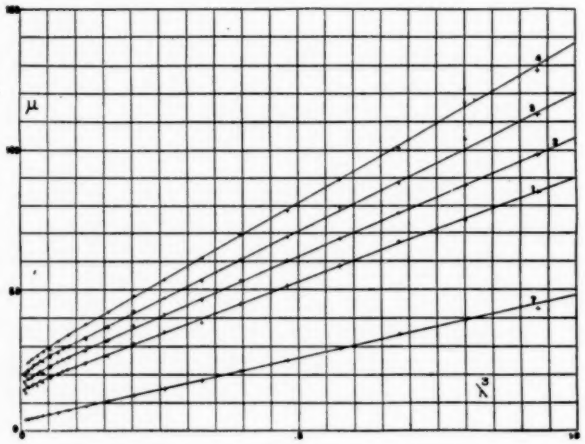



Fig. 1.

In these graphs the curves are numbered as follows:

1. Benzene,
2. Toluene,
3. Xylene,
4. Mesitylene,
5. Heptane,
6. Cyclohexanol,
7. Water.

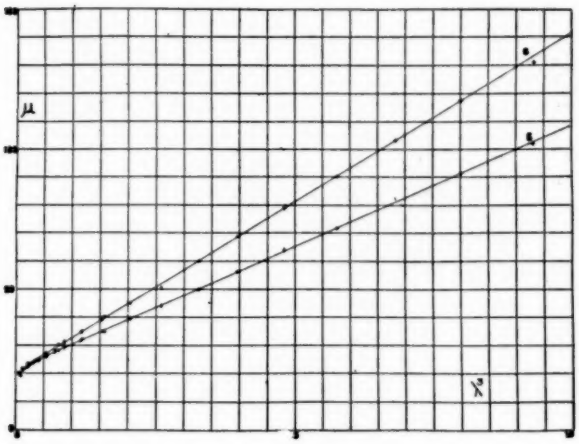



Fig. 2.

TABLE I.

| λ in Ångstroms. | Benzene. | Toluene. | Xylene. | Mesity-lene. | Heptane. | Cyclo-hexanol. | Water. |
|---|---|---|---|---|---|---|---|
| .2137..... | 13.48 | 16.53 | 19.60 | 20.74 | 19.03 | 19.36 | 3.77 |
| .2455.. ..... | 15.40 | 18.70 | 21.15 | 24.27 | 21.55 | 21.39 | 4.01 |
| .2782..... | 15.95 | 18.91 | 22.27 | 25.44 | 23.36 | 22.18 | 4.25 |
| .3109..... | 16.15 | 20.31 | 23.76 | 26.50 | 23.34 | 23.27 | 4.68 |
| .3436..... | 17.34 | 20.52 | 24.45 | 28.14 | 24.37 | 24.88 | 5.38 |
| .3763..... | 18.80 | 22.38 | 25.90 | 28.89 | 25.68 | 27.08 | 5.87 |
| .4089..... | 20.25 | 24.57 | 27.79 | 31.66 | 27.24 | 28.61 | 6.39 |
| .4416..... | 21.85 | 26.04 | 29.83 | 33.88 | 29.40 | 31.36 | 7.17 |
| .4905..... | 24.21 | 28.77 | 32.64 | 38.00 | 32.25 | 35.24 | 8.83 |
| .5394..... | 26.75 | 31.95 | 36.62 | 41.93 | 35.00 | 40.21 | 10.62 |
| .5883..... | 30.85 | 37.19 | 42.22 | 47.88 | 39.41 | 45.13 | 12.62 |
| .6371..... | 35.00 | 41.10 | 46.91 | 53.58 | 44.03 | 51.58 | 14.96 |
| .6859..... | 38.27 | 46.32 | 53.08 | 61.03 | 49.78 | 59.89 | 17.91 |
| .7346..... | 44.80 | 53.17 | 60.63 | 69.46 | 56.55 | 68.83 | 21.32 |
| .7833..... | 51.28 | 60.32 | 68.45 | 78.12 | 63.98 | 79.08 | 25.09 |
| .8319..... | 58.34 | 67.75 | 79.37 | 89.52 | 71.59 | 90.15 | 29.28 |
| .8804..... | 66.79 | 77.31 | 88.12 | 100.71 | 82 53 | 103.33 | 34.13 |
| .9289..... | 74.61 | 87.21 | 103.74 | 116.62 | 91.44 | 117.81 | 39.51 |
| .9773..... | 84.99 | 98.47 | 112.50 | 128.23 | 102.15 | 130.89 | 43.20 |
| The following observations were taken on 10 cm. tubes. In the plots they are represented by circles. | | | | | | | |
| .1899..... | 14.69 | 17.50 | 20.21 | | 20.14 | 19.80 | |
| .2389..... | 15.60 | 18.69 | 21.70 | | 21.44 | 21.61 | |
| .2880..... | 16.77 | 20.00 | 23.30 | | 22.96 | 23.12 | |
| .3289..... | 17.94 | 21.22 | 24.81 | | 24.22 | 24.54 | |
| .3779..... | 19.47 | 23.16 | 26.91 | | 26.04 | 27.16 | |
| .4269..... | 21.15 | 25.34 | 29.36 | | 28.37 | 30.16 | |
| .4872..... | 23.89 | 28.41 | 32.96 | | 31.46 | 34.47 | |
| .5362..... | 26.73 | 31.71 | 36.80 | | 35.01 | 39.01 | |

That portion of the curve represented by $\lambda > .25$ Å. is a straight line in every case, and therefore we can write $\mu = A + B\lambda^3$. We thus obtain the following table of constants:

| No. of Curve. | Substance. | *A*. | *B*. |
|---|---|---|---|
| 1 | $C_6H_6$ | 15.3 | 74.9 |
| 2 | $C_6H_5CH_2$ | 19.0 | 85.3 |
| 3 | $C_6H_4(CH_2)_2$ | 21.7 | 98.3 |
| 4 | $C_6H_3(CH_2)_3$ | 24.2 | 113.6 |
| 5 | $C_7H_{16}$ | 21.5 | 87.3 |
| 6 | $C_6H_{12}O$ | 20.5 | 121.0 |
| 7 | $H_2O$ | 3.5 | 44.5 |

Theoretically we are now in a position to test the additive law, for the first four substances were so chosen as to give constant differences. Making these subtractions, we derive these values of *A* and of *B* for $CH_2$:

| Difference. | *A*. | *B*. |
|---|---|---|
| 2–1 | 3.7 | 10.4 |
| 3–2 | 2.7 | 13.0 |
| 4–3 | 2.5 | 15.3 |

The natural conclusion from this table alone is that the additive law does not hold. In this, however, we are not justified. The method of calculation employed groups all the errors of observation into the small differences which we wish to compare, thus greatly increasing the percentage error. Fortunately we have at our disposal other methods of calculation which eliminate this objection. We shall revert to the constants for $CH_2$ after we have calculated those for carbon, oxygen and hydrogen.

From the graphs a value of the molal absorption coefficient was taken for each substance at each wave-length, and from these the mass absorption coefficients for the elements involved were calculated. The method of calculation involves as many substances as possible, and also division by large numbers, thus minimizing the error. Thus we chose to add the molal absorption coefficients of benzene ($C_6H_6$), toluene ($C_7H_8$), mesitylene ($C_9H_{12}$), and water ($H_2O$), and from the sum subtract the molal absorption coefficients of heptane ($C_7H_{16}$) and cyclohexanol ($C_6H_{12}O$). The remainder is nine times the molal absorption coefficient of carbon. Division by 108 gives the mass absorption coefficient directly.

In a similar way we calculate the mass absorption coefficient of hydrogen by adding the molal absorption coefficients of benzene, toluene, xylene, mesitylene and heptane, and from the sum subtracting thirty-seven times the molal absorption coefficient of carbon as found above, and dividing the remainder by $52 \times 1.008$.

For oxygen we subtract twice the molal absorption coefficient of hydrogen from that found for water and divide the remainder by 16.

The values taken from the graphs are found in Table II.; the calcu-

lations are summarized in Table III., and graphed in Figs. 3, 4, and 5 as functions of $\lambda$ and of $\lambda^3$.

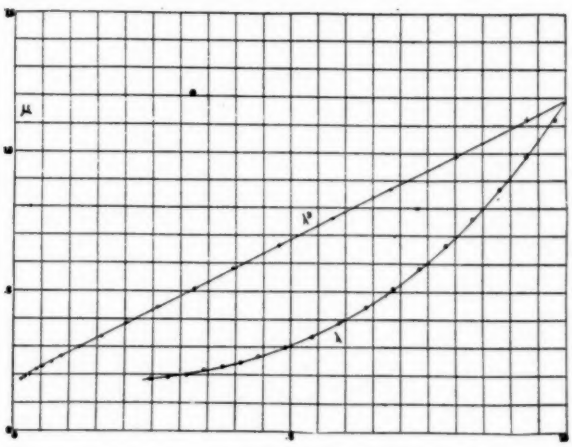



Fig. 3.

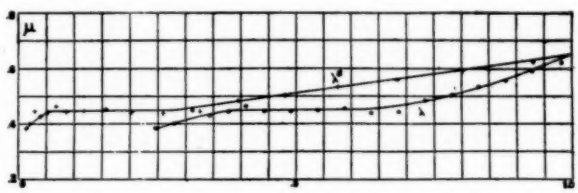



Fig. 4.

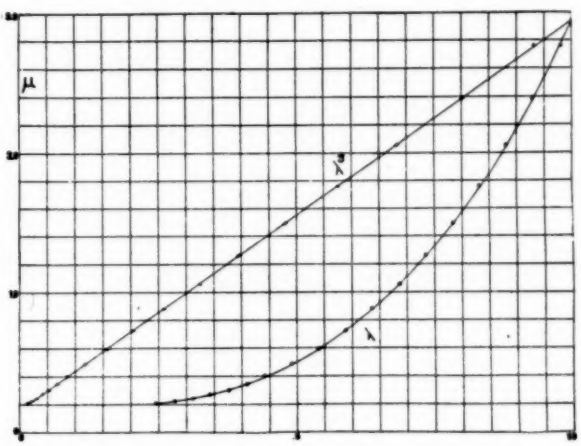



Fig. 5.

TABLE II.

| λ in Ångstroms. | Benzene. | Toluene. | Xylene. | Mesity-lene. | Heptane. | Cyclo-hexanol. | Water. |
|---|---|---|---|---|---|---|---|
| .2455 | 15.6 | 18.75 | 21.75 | 24.5 | 21.55 | 21.45 | 4.12 |
| .2782 | 16.45 | 19.70 | 22.90 | 25.4 | 22.48 | 22.65 | 4.40 |
| .3109 | 17.37 | 20.7 | 24.0 | 26.55 | 23.60 | 24.2 | 4.80 |
| .3436 | 18.45 | 21.85 | 25.35 | 28.15 | 24.85 | 25.45 | 5.30 |
| .3763 | 19.38 | 23.00 | 26.7 | 29.55 | 26.15 | 26.85 | 5.80 |
| .4089 | 20.47 | 24.35 | 28.35 | 31.55 | 27.7 | 28.85 | 6.50 |
| .4416 | 21.90 | 26.15 | 30.3 | 33.90 | 29.40 | 31.10 | 7.37 |
| .4905 | 24.13 | 28.70 | 33.25 | 37.35 | 32.00 | 34.75 | 8.75 |
| .5394 | 26.95 | 32.0 | 37.05 | 41.90 | 35.45 | 39.40 | 10.40 |
| .5883 | 30.50 | 36.1 | 41.7 | 47.3 | 39.65 | 44.9 | 12.55 |
| .6371 | 34.55 | 40.8 | 46.85 | 53.6 | 44.35 | 51.60 | 15.00 |
| .6859 | 39.25 | 46.35 | 53.6 | 60.65 | 49.85 | 59.15 | 17.87 |
| .7346 | 44.85 | 52.65 | 60.65 | 69.1 | 56.45 | 68.5 | 21.20 |
| .7833 | 51.15 | 59.75 | 69.1 | 78.6 | 63.75 | 78.7 | 25.00 |
| .8319 | 58.25 | 68.0 | 78.45 | 89.1 | 72.0 | 90.35 | 29.25 |
| .8804 | 66.20 | 77.15 | 89.0 | 101.0 | 81.2 | 103.4 | 34.05 |
| .9289 | 75.05 | 87.35 | 100.7 | 114.25 | 91.6 | 117.9 | 39.45 |
| .9773 | 84.98 | 98.8 | 113.85 | 129.1 | 103.25 | 134.1 | 45.50 |

TABLE III.

*Mass Absorption Coefficients.*

| λ in Ångstrom Units. | Carbon. | Hydrogen. | Oxygen. |
|---|---|---|---|
| .2455 | .185 | .382 | .209 |
| .2782 | .193 | .407 | .223 |
| .3109 | .200 | .445 | .244 |
| .3436 | .217 | .425 | .278 |
| .3763 | .229 | .441 | .307 |
| .4089 | .244 | .462 | .348 |
| .4416 | .267 | .442 | .405 |
| .4905 | .298 | .446 | .491 |
| .5394 | .337 | .452 | .593 |
| .5883 | .388 | .439 | .729 |
| .6371 | .444 | .435 | .883 |
| .6859 | .510 | .441 | 1.061 |
| .7346 | .582 | .482 | 1.264 |
| .7833 | .667 | .499 | 1.496 |
| .8319 | .761 | .532 | 1.761 |
| .8804 | .868 | .553 | 2.058 |
| .9289 | .987 | .589 | 2.391 |
| .9773 | 1.121 | .617 | 2.766 |

The curves in Figs. 3, 4 and 5 again emphasize the linear relationship between $\lambda^3$ and $\mu$. The range in the case of hydrogen extends only down to $\lambda = 0.65$ Å. From these curves we obtain the constants for the straight line portion expressed by $\mu = A + B\lambda^3$ as follows:

| Element. | *A*. | *B*. |
|---|---|---|
| Hydrogen | .37 [.309] | .28 |
| Carbon | .18 [.175] | 1.01 [1.035] |
| Oxygen | .16 [.165] | 2.785 [2.644] |

The values in the square brackets are taken from Hewlett[1] who used carbon in the form of graphite, and liquid oxygen. This remarkable agreement is in direct contradiction to the results of Auren to which we referred in the beginning of this article and constitute a proof of the additive law. We are now in a position to calculate the constants for molar absorption coefficients of $CH_2$. Thus:

| | | *A.* | *B.* |
|---|---|---|---|
| 1 | $\frac{\mu C_6H_{12}O - \mu O}{6}$ | 2.99 | 12.75 |
| 2 | $\frac{\mu C_7H_{16} - 2(\mu H)}{7}$ | 2.97 | 12.39 |
| 3 | $\frac{\mu C_6H_{12}O + \mu C_7H_{16} - \mu H_2O}{13}$ | 2.96 | 12.6 |
| 4 | $\frac{\mu C_6H_6}{6} + \mu H$ | 2.92 | 12.76 |
| 5 | $\mu C + 2\mu H$ | 2.90 | 12.6 |

The first three involve carbon only in the aliphatic condition (since a saturated benzene ring resembles a paraffin in its properties); the fourth method involves only aromatic carbon, and the fifth involves both kinds.

We must conclude therefore that the absorption coefficients of aliphatic carbon, aromatic carbon, and graphitic carbon are the same for wavelengths less than 1 Å.

CHEMICAL AND PHYSICAL LABORATORIES
UNIVERSITY OF CALIFORNIA
August 8, 1922

[1] C. W. Hewlett, PHYS. REV., *17*, 284 (1921).

# EFFECTS OBTAINED WITH AN ALTERNATING CURRENT SENT THROUGH A CAPILLARY ELECTROMETER.

By R. D. Kleeman and D. T. Simonds.

Abstract.

**Capillary electrometer.**—(1) *Comparison of effects of direct and alternating voltages.* A special form of electrometer was used, in which a horizontal capillary whose bore gradually increased from the middle toward both ends, connected a reservoir of mercury and a reservoir of a saturated solution of mercurous sulphate. In agreement with well-known results, when a direct current was sent from the solution to the mercury, the pressure required to keep the end of the mercury thread at the middle of the capillary increased with the voltage to a maximum of about 24 cm. at 1.1 volts, whereas with a current in the opposite direction, the negative pressure required increased to a maximum of only 4 cm. for 0.2 volt which was the limit for consistent measurements because of the generation of gas. An alternating current was found to move the thread in the same direction as a direct current from the solution. This is not due to the direct current component produced by the rectifying action of the electrometer, for this component is in the opposite direction and when it was eliminated by the use of a condenser still larger deflections were obtained, the pressure readings increasing more or less linearly with the voltage up to 10.5 cm. for 1.15 volts and then remaining constant to 1.4 volts. The same results were obtained with frequencies up to 200 as with 60 cycles. (2) *Transition layer theory*, which had been suggested in explanation of the e.m.f. of a voltaic cell, also explains these results, at least better than the Helmholtz theory. It is assumed that between the mercury and the solution is a transition layer in which the positive and negative ions are partly segregated. An electrical current passing through the layer would change the extent of this segregation and hence alter the corresponding difference of potential and potential energy of the layer. As a consequence, the impressed negative voltage required to neutralize the normal transition e.m.f. $E$ is not numerically equal to $E$, as assumed by the Helmholtz theory, but somewhat greater; and when an alternating current passes through, the decrease in electrical potential energy during half a cycle should be quite different in value from the increase during the other half cycle. These conclusions are in agreement with the above results.

EXPERIMENTS were carried out to investigate the effects of an alternating current sent through a special form of capillary electrometer. This consisted of a more or less horizontal capillary tube $A$ whose diameter gradually increased from its middle point towards the ends, which terminated in two reservoirs $B$ and $C$, as shown diagrammatically in Fig. 1. The reservoir $B$ contained a small quantity of mercury which made contact with one of the electrodes, and on top of which floated a saturated solution of mercurous sulphate containing one vol-

ume of sulphuric acid to seven volumes of water. The reservoir *C* contained only mercury which made contact with the other electrode, and a thread of which met the solution about half way in the capillary tube. The interfacial surface tension $\lambda$ of the mercury and solution exerts a pressure

$$\frac{2\pi r\lambda}{\pi r^2} = \frac{2\lambda}{r}$$

per cm.$^2$ of the cross-section $\pi r^2$ of the tube in the direction of the mercury thread. This is counterbalanced by the pressure of the mercury in the reservoir *C*, whose magnitude could be varied by varying the inclination of the apparatus, and thus the mercury-solution interface could be kept at any desired part of the capillary tube. The interface was usually in equilibrium under the action of a pressure of about 4 cms. of mercury. Additional pressure, positive or negative, could be applied to the mercury if desired by means of a manometric arrangement *D* which consisted of a reservoir of mercury *d* which could be raised or lowered at will. This changed the pressure of the air in the part *e* of the tube connected with the reservoir *C*. The position of the mercury-solution interface was observed by means of a microscope having a scale in the eye-piece.

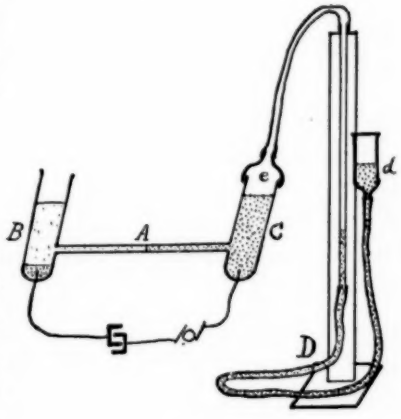



Fig. 1.

It was found that an alternating current sent through the system gave rise to a motion of the mercury-solution interface towards the thread of mercury. This was in the direction of an increase in the diameter of the capillary tube, and the result therefore shows that the current increased the interfacial surface tension since it exerts the pressure $2\lambda/r$ towards the mercury. The interface would accordingly move to a point so that the value of the fraction $2\lambda/r$ would be the same as before.

The displacement of the interface was found to be in the same direction as that obtained with a direct current passing from the solution to the mercury. It was thought therefore that the effect obtained with an alternating current might be caused by it becoming partly rectified. It was found however that the direct current component which existed flowed in the direction from the mercury to the solution, and therefore really decreased the effect of the alternating current. Accordingly when a condenser was put into the circuit to cut out the direct current

component the deflections obtained increased in the order of 25–50 per cent. depending on the magnitude of the current. The significance of this result will be discussed later.

Instead of observing the deflection produced by a given current, we may observe the pressure necessary to apply to the mercury surface in the reservoir $C$ which will keep the interface in position, and thus obtain results of a more definite nature. A set of measurements was carried out in this way with a condenser of two microfarads capacity in the circuit to cut out the direct current component, and using an alternating current of sixty cycles per second. The results obtained are shown by the curve $A$ in Fig. 2, which indicates the relation between the alternating

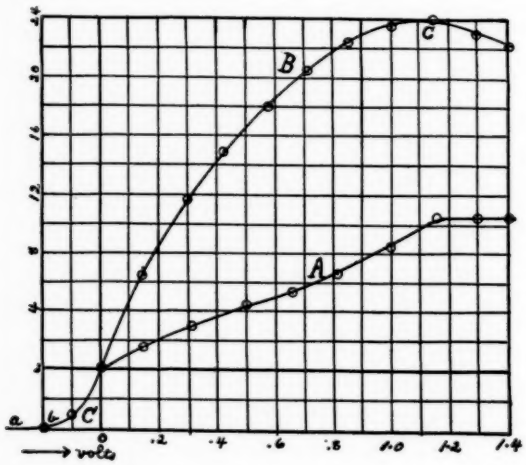



Fig. 2. Pressure $P$ in centimeters of mercury as a function of applied voltage.

e.m.f. between the terminals of the electrometer and the pressure applied to keep the interface in position. It will be seen that this pressure increases very approximately linearly with the e.m.f. between the electrodes up to a pressure of about 10 cm. of mercury, beyond which it is little affected by the magnitude of the e.m.f. applied.

On sending a direct current from the solution to the mercury results were obtained represented by the curve $B$ in Fig. 2. This curve is the same in form as that obtained previously by various investigators. It has a maximum at a pressure of about 23 cms. of mercury, which corresponds to 1.2 volts. The curve obtained with an alternating current has a maximum at a pressure of about 10 cms. of mercury at about the same voltage. On sending a direct current from the mercury to the solution the curve $C$ was obtained. The part $ab$ of this curve is rather uncertain on account of the inconsistent readings obtained. Small

bubbles of gas seemed to form, which had the effect of obstructing the motion of the thread of mercury, and hence the transmission of pressure. Thus a considerable pressure could often be applied without moving the interface past a point where bubbles had been formed. Occasionally it was therefore necessary to drive out the thread of mercury and replace it by a fresh one before continuing the observations. It should be mentioned that when an alternating current was used the results obtained were quite consistent, and thus were not affected by the inconsistencies obtained with a direct current in one direction.

Experiments were also carried out to see whether the nature of the curve obtained with an alternating current depended on the number of its cycles per second. Using a rotary converter the number of cycles was varied from that just giving a steady interface up to about 200 cycles per second. But no appreciable change in the pressure applied was observed on keeping the voltage between the terminals of the electrometer constant.

The curve of the nature of the curve *B* in Fig. 2 has been carefully studied by numerous observers using different kinds of solutions. It usually indicates a maximum which is situated approximately symmetrically with respect to the two portions of the curve into which it is divided by the maximum. The curve of the nature of the curve *C* in Fig. 2 has however scarcely received any attention, possibly through encountering experimental difficulties. The effect of an alternating current appears not to have been previously investigated. Since it produces an effect, it is of importance to remember this when using the capillary electrometer in certain investigations, such as measuring the electric currents between animal tissues, in which the effects obtained may not be entirely due to direct currents.

The curve *B* has been explained by Helmholtz on the supposition that the mercury and solution form the opposite plates of a charged condenser, the mercury being positively and the solution negatively charged. Since the value of the potential energy of every system tends to become a minimum, the introduction of electrical potential energy into the mercury-solution interface would tend to decrease its surface tension below that it would otherwise possess. Now when a current is passed from the solution to the mercury the attending fall of potential would give rise to a partial discharge of the condenser, and a corresponding increase in the surface tension. When the condenser is completely discharged the surface tension is at a maximum, which corresponds to the point *c* in Fig. 2. On further increasing the current the condenser charges up in the opposite direction, and hence the surface tension is decreased

correspondingly. Thus the curve obtained should be symmetrical about the pressure axis through the point $c$. This is however only approximately realized.

If a current is sent in the opposite direction the charge on the condenser is increased, and the surface tension would be correspondingly decreased, as is shown by the curve $C$ in Fig. 2. For a certain value of the current the surface tension should therefore be zero. For larger currents the interface would behave simply as an electric condenser. It would therefore tend to move in a direction increasing its capacity, or towards a wider part of the capillary tube. The magnitude of the tendency of this motion and its direction would therefore depend on the location of the interface in the capillary tube. This would in part explain the inconsistent results obtained in this case.

Let us next examine what should happen according to Helmholtz's theory when an alternating current is sent through a capillary electrometer. Let $\lambda_0$ denote the surface tension of the interface that would exist if no separation of electrical charges occurred or no charged condenser existed. The actual surface tension would then be given by $(\lambda_0 - kE^2)$ where $E$ denotes the difference of potential of the condenser associated with the layer, and $k$ a constant. Therefore if the difference of potential of the condenser is decreased by $e$, the surface tension will be increased by $k(2Ee - e^2)$. If on the other hand it is increased by $e$, the surface tension is decreased by $k(2Ee + e^2)$. Thus the decrease would be greater than the increase. Hence if an alternating e.m.f. be applied to the electrometer, and this gives rise to equal and opposite changes in the potential of the condenser, the surface tension should decrease. But the opposite is obtained by experiment. We must therefore suppose that the resistance of the interface is greater when the current flows from the solution to the mercury than when flowing in the opposite direction, so that $e$ will have a greater value in the former case than in the latter. The average potential difference of the mercury solution interface of small area will then be less when an alternating current is flowing than that of the interface of large area, which would give rise to a direct current component flowing in the direction from the mercury to the solution at the small interface. This fits in with the observations.

But Helmholtz's theory does not explain, or even suggest, the mechanism by means of which the charged interfacial condenser is produced and maintained. It therefore does not lend itself to an extended analysis to explain the various facts. The theory of the e.m.f. of a voltaic cell proposed by the writer[1] is more fundamental in character, and by means

[1] PHYS. REV. 20, 174, 1922.

of it the properties of the capillary electrometer may be explained along more fundamental lines.

According to this theory a liquid transition layer exists at the interface of a metal and liquid in which the density gradually changes from one side of the layer to the other. Due to an asymmetrical dissociation of molecules into ions in the layer, the different rates of diffusion of the positive and negative ions, etc., a partial segregation of the positive and negative ions will take place in the layer.

This will be attended by a charging up of the plate till electrical equilibrium is reached. This is illustrated diagrammatically by Fig. 3 for the case that a surplus of positive ions exists near the surface of the metal. An electric field will accordingly exist across the transition layer. Now let us consider the effect of a direct current passed in the direction from *a* to *b* in Fig. 3. It will evidently initially decrease the potential difference of the transition layer. But since the equilibrium between the ions is associated with a certain fall of potential across the layer, further segregation of ions will take place to counteract this change of potential. If this change is small the difference of potential of the layer might ultimately attain its former value. But it is evident that if the current is increased indefinitely the change of potential across the layer cannot be maintained the same since the amount of segregation of ions that can take place is limited. Hence the *total* potential difference should eventually become zero and then change its sign. Thus the transition layer would behave similarly to the Helmholtz condenser. But the *impressed* fall of potential across the layer, due to the current flowing in the case that the *total* fall of potential is zero, is not necessarily equal to the fall of potential in the opposite direction when there is no current flowing, as follows from the Helmholtz theory. Thus if a fall of potential is impressed upon the layer equal and opposite to its original potential, the resultant segregation of ions would, in the way explained, tend to restore a part of the original fall of potential. It follows therefore that the *impressed fall of potential*, in the case that the *total fall* is zero, will be *greater than* the original fall of potential across the layer. This result would explain why the calculation of the various voltaic combinations, based on the results obtained on the Helmholtz assumption that the e.m.f. between mercury and a solution is equal to the impressed e.m.f. when the surface tension is a maximum, which corresponds to the total e.m.f. being zero, does not give results agreeing with those obtained by

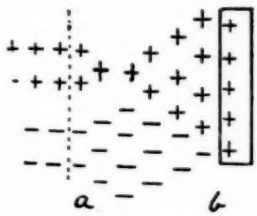


Fig. 3.

other methods. This is of course also a point of importance in connection with the determination of the *absolute* potential difference between a metal and a solution.

Next let us suppose that a current is sent through a transition layer in the same direction as its fall of potential, which would initially give rise to an increase in the total fall of potential. Therefore, since the equilibrium of the ions in the layer is associated with a definite fall of potential, an increase in this potential would give rise to a decrease in the segregation of the ions in order to render the increase in the total difference of potential as small as possible. Hence for a certain impressed fall of potential practically no segregation of ions would take place. For larger impressed potentials, segregation would take place in a reverse manner.

Now the observed surface tension of the interface we have seen is equal to the difference between its ideal surface tension, or that which it would possess if no electrical conditions existed, and the electrical potential energy associated with the layer. Hence in the foregoing case the surface tension would gradually decrease as the impressed fall of potential is increased, and may even become zero and then change sign. In the preceding case which corresponds to an impressed potential in the opposite direction, the surface tension would increase with increased potential, reach a maximum, and then decrease. The facts, as far as they go, agree with these deductions.

It will be evident now that on sending an alternating current through the interface the decrease in electrical potential energy when the current passes in one direction need not be equal to the increase when passing in the reverse direction, in fact, it is easy to see that these quantities may have very different values. According to the experimental results shown by the curve *A* obtained with direct currents the decrease in the former case, which corresponded to an impressed fall of potential opposite to the natural fall of potential of the layer, is much larger than the increase in the latter case. A difference of potential would accordingly exist between the two mercury-solution interfaces of the electrometer since the current densities across them have different values. This is a true voltaic difference of potential according to the theory proposed, it should be noted, and is not due, as might be supposed, to the layer posessing asymmetrical resistances with respect to the direction of the current, or other asymmetrical properties not depending on the segregation of ions in the layers.

The experiments on the whole have shown that the e.m.f. between a metal and a solution is located largely if not altogether in the vicinity

of their interface. In this region a segregation of ions would take place according to a theory proposed previously, which would necessarily be attended by the production of an e.m.f. This would well explain in a general way the effects attending the passage of a direct or alternating current across the interface.

We wish to express our thanks to the General Electric Company for providing part of the time and some of the apparatus to carry out the foregoing investigation.

UNION COLLEGE,
SCHENECTADY, N. Y.,
August 16, 1922.

# THEORY OF SOLUBILITY.

By Joel H. Hildebrand.

Abstract.

**Theory of solubility.**—(1) *Statement.* The theory of solubility advocated by the writer in a series of papers is restated. Raoult's law will be obeyed by any liquid mixture in which the internal forces of attraction and repulsion do not change with changing composition of the mixture. When this condition holds, the solubility of a gas may be calculated approximately from its saturation pressure, and the solubility of a solid from its melting point and heat of fusion. The above condition can exist only (*a*) when the components in the pure liquid state have the same internal pressures; (*b*) when the different molecules are relatively symmetrical or non-polar; (*c*) when the tendency to form chemical compounds is absent. Differences in either internal pressure or polarity alone produce approximately proportional positive deviations from Raoult's law and decreased solubilities. Tendencies towards chemical combination produce negative deviations and increased solubilities. Internal pressure is defined as $T(\partial P/\partial T)_v$; relative values can be deduced from other data, especially the solubility relations themselves. Polarity is indicated by dielectric constant, etc., and depends on the symmetry and the chemical constitution of the molecule. Chemical combinations are difficult to predict, but, in general, occur most frequently between polar molecules, especially those which can be regarded as positive and negative, or basic and acidic, respectively. (2) *Discussion of criticism by Kunerth.* Kunerth has severely criticized this theory, concluding that Raoult's law and internal pressures are practically useless as a basis for predicting the solubilities of gases. This paper points out that most of the solvents Kunerth uses are highly polar. A table of gas solubilities in non-polar solvents is given. The solvents are arranged according to increasing internal pressure, and the table includes the solubility as calculated approximately by the aid of Raoult's law. Though the solubilities cover a wide range the agreement with the theory is good.

IN a series of papers by the author and his collaborators during the past six years[1] a theory of solubility has been advocated which may be briefly summarized as follows.

1. The tendency of a given molecule to escape from a solution into some other phase will be independent of the composition of the solution whenever that molecule is subject to the same attractive and repulsive forces in the solution as it is in its own pure liquid. If the number of molecules of the species $X_1$ in the solution is the fraction $N_1$ of the total number of molecules of all species present, then their tendency to escape from the

[1] Hildebrand, J. Am. Chem. Soc., *38*, 1452 (1916); *39*, 2297( 1917); *41*, 1067 (1919); Hildebrand and Jenks, ibid., *42*, 2180 (1920); Hildebrand and Buehrer, ibid., *42*, 2213 (1920); Hildebrand, ibid., *43*, 500 (1921); Hildebrand and Jenks, ibid., *43*, 2172 (1921).

solution into some other phase, $f_1$, is the same fraction of their tendency to escape from their own pure liquid, $f_1^0$, viz., $f_1 = f_1^0 N_1$. For the species $X_2$, $X_3$, etc., we would have the similar expressions, $f_2 = f_2^0 N_2$, $f_3 = f_3^0 N_3$, etc. When the escaping tendency or fugacity [1] is measured by the vapor pressure and the vapor is assumed to obey the gas laws, this becomes $p_1 = p_1^0 N_1$, which is the well-known law of Raoult.

2. When the above condition holds $N_1$ may be regarded as the solubility of $X_1$ in the solution for a given value of $f_1/f_1^0$. The solubility of a vapor at any arbitrary pressure, $p_1$, can, therefore, be calculated from its saturation pressures, $p_1^0$. Where the substance is a gas above its critical temperature an approximate estimate of the solubility may still be made by extrapolating above the critical temperature to get a fictitious value for $p_1^0$. When the solubility of a solid is being considered, $f_1/f_1^0$ can be calculated from the melting point and the heat of fusion.

3. The above relations can be expected to hold only under the following conditions: (*a*) the components when in the state of pure liquids must have equal internal pressures or cohesions; (*b*) the fields of force around the molecules of the components must be sufficiently symmetrical or non-polar; (*c*) the molecules of different species must not exert abnormally large attractions upon each other such as appear in the tendency to form chemical compounds.

4. Where conditions (*b*) and (*c*) hold, differences in internal pressure lead to approximately proportional increases in escaping tendency and decreases in solubility.

5. Differences in polarity in the absence of chemical combination have a corresponding effect.

6. The tendency to chemical combination between the components leads to decreased escaping tendency and hence increased solubility.

7. Internal pressure has been defined as $T(\partial P/\partial T)_v$, one of the terms in the thermodynamic equation of state. Its value may be calculated from the coefficients of expansion and compressibility. Approximate relative values may also be obtained by the aid of other data, such as surface tensions and heats of vaporization.

8. Relative internal pressures can also be deduced from solubility data themselves since it is possible thereby to arrange non-polar substances in a series in which the more widely separated are any pair of substances, the more strongly does their solution deviate in a positive direction from Raoult's law.

9. Polarity of a molecule or a group within a molecule can be related to dielectric constant and other physical properties, also to symmetry and chemical nature.

[1] G. N. Lewis, Proc. Am. Acad., *37*, 49 (1901); Z. physik. Chem., *38*, 205 (1901).

10. The prediction of chemical combination in connection with solubility offers the same difficulties that it does elsewhere, and is a very complicated problem. In general, however, it occurs most frequently between polar substances, and between substances which may be regarded as respectively positive and negative, or basic and acidic.

The writer claims but a small portion of credit for this comprehensive theory. So important a problem as solubility has not escaped attention from a host of investigators, and nearly all parts of the theory above outlined have been separately stated more or less clearly by others, and I have tried to indicate them as adequately as possible in my series of papers. The chief cause of failure hitherto has been the neglect of some of these factors while studying the others.

In a paper in THE PHYSICAL REVIEW entitled "Solubility of $CO_2$ and $N_2O$ in certain solvents" Professor Wm. Kunerth[1] has recently made such sweeping objection to the theory here outlined as to call for some words of explanation and reply.

This investigator, upon comparing the solubilities of $CO_2$ and $N_2O$ in a number of solvents with the solubility calculated from Raoult's law, concludes that "the procedure of Dolezalek" who first used Raoult's law for this purpose, attempting to correct for deviations from the gas laws by using $p^0 + a/v^2$ from the van der Waals equation in place of $p^0$, "is utterly worthless for predicting solubility of gases in liquids."

Now it would seem to the writer that a procedure is not utterly worthless which can yield even an approximate prediction of so important a property as solubility, especially if we are able to say which substances will approximate most closely to our prediction. According to the theory above outlined this will be the case with non-polar substances whose pure liquid phases have equal internal pressures. We will therefore expect better agreement with non-polar gases like nitrogen and methane than with somewhat polar gases like carbon dioxide, ammonia and hydrogen chloride, and better agreement with the less polar solvents such as hexane, carbon tetrachloride and ethylene bromide, than with water, the alcohols, acids and amines. Furthermore, we will expect that the value for solubility got by the aid of Raoult's law will be most closely approached as the internal pressure of the solvent corresponds to that of the condensed gas.

A fair test of the theory should, of course, have due regard to the conditions stated. In my first paper on the subject I stated "(1) Raoult's law should be obeyed by mixtures of non-polar liquids having the same internal pressures; (2) non-polar liquids of different internal pressures

[1] Kunerth, PHYS. REV., *19*, 512 (1922).

will show greater vapor pressures in the mixture than would be expected from Raoult's law; (3) the same holds true for mixtures of polar with non-polar liquids; (4) mixtures of polar liquids may show either positive or negative deviations from Raoult's law, but in most cases the latter will predominate; (5) these deviations will modify the predictions of solubility for gases, liquids, and solids based upon Raoult's law alone, the solubilities being greater where negative deviations occur and *vice-versa*." In the same paper a section of four pages is devoted to the discussion of polarity, and dielectric constants are given in the table of internal pressures. I have also been careful in later papers, when examining relatively non-polar systems because of their greater regularity of behavior, to limit my conclusions to this class. In spite of this Kunerth states the internal pressure theory without reference to this limitation. He proceeds to test the internal pressure theory on the basis of solubilities in a series of twenty-one solvents, of which only eight have dielectric constants as low as 5, and amyl acetate, though having a dielectric constant of only 4.8, contains the highly polar—COO—group. In my own tests of the effect of internal pressure I have seldom used substances with dielectric constants above 5, or containing groups commonly recognized by chemists as highly polar, such as hydroxyl, carboxyl, amino and aldehyde. I can agree with Kunerth when he says that so far as his own table goes "its indications are that the solubility of gases in liquids is connected with polarity rather than with . . . internal pressures," because he has chosen mainly polar solvents, but for this very reason his data do not furnish an adequate basis for a general denial of the connection between internal pressure and solubility in cases of low polarity.

In reference to my original table for the solubilities of $H_2$, CO, $N_2$, $CH_4$, $C_2H_6$, $C_2H_4$, $CO_2$ and $NH_3$ in various solvents, some of them polar, I said "the greatest uncertainty is where the polar solvents are concerned. This is not surprising, as the uncertainties are necessarily greater in such cases on account of our inability to determine how much of the internal pressure is due to the polarity. Carbon dioxide is obviously, from its chemical reactivity, much more polar than the gases previously mentioned, and additional uncertainties are thus introduced, though a distinct increase in solubility in the more polar solvents is evident." In spite of this, Kunerth implies that I based by discussion entirely upon internal pressure, and states that "the conclusion which Hildebrand draws is very obviously not warranted."

Now let us see whether this is true. Considering only the substances of low polarity, having dielectric constants not over 5, we can make a

table of gas solubilities, using data quoted in my original paper for carbon monoxide, nitrogen and methane, those given by Kunerth for carbon dioxide and nitrous oxide, some data for chlorine by Taylor, of this laboratory, and not heretofore published, and for phosgene by Atkinson, Heycock and Pope.[1]

The solvents are arranged in order of increasing internal pressure, using the values of $T(\partial P/\partial T)_v$ given in a previous paper, which order is confirmed by solubility data given in other papers for various solids. The position of carbon bisulfide is chosen in accordance with the latter basis. At the top of the table are given values of $1/p^0$, where $p^0$, is the saturation pressure, extrapolated in the case of CO, $N_2$ and $CH_4$ by the aid of the straight line plot of log $p$ against $1/T$. According to Raoult's

*Solubility in Mol—Per Cent.*

| | CO. | $N_2$. | $CO_2$. | $N_2O$. | $CH_4$. | $Cl_2$. | $COCl_2$. | Internal Pressure. |
|---|---|---|---|---|---|---|---|---|
| Temp. | 20° | 20° | 20° | 20° | 25° | 0° | 24° | 20° |
| Raoult's law, $1/p^0$ | 0.11 | 0.10 | 1.78 | 1.81 | 0.32 | 27.3 | 55.0 | |
| Heptane | | | | | | 27.0 | | 2,970 |
| Hexane | | | | | 0.31 | | | 2,970 |
| Xylene | 0.089 | 0.061 | 1.02 | | 0.26 | | 53.0 | 3,690 |
| Carbon tetrachloride | | | 1.00 | | | 29.6 | | 3,690 |
| Toluene | 0.077 | 0.053 | 1.08 | | 0.21 | | 53.0 | 3,830 |
| Chloroform | 0.063 | 0.043 | 1.23 | 1.82 | | | | 3,880 |
| Benzene | 0.061 | 0.041 | 0.94 | | | | | 4,100 |
| Ethylene bromide | | | 0.82 | 1.00 | | | | 4,760 |
| Carbon bisulfide | 0.020 | 0.013 | 0.23 | | | | | |

law $1/p^0$ should give the solubility of the gas at 1 atmosphere pressure. According to our theory this should be approached most nearly in the solvents of internal pressure equal to that of the condensed gas. According to the third paper of our series the internal pressures of CO and $N_2$ are lower than those of any of the liquids given in the table, so that the best solvent, xylene, has a solvent power distinctly lower than $1/p^0$, while the solvent powers of the other liquids decrease regularly with their increasing internal pressures. Methane, as we might expect, dissolves in hexane as given by $1/p^0$, within the limit of error, becoming less soluble as we descend to xylene and toluene. We might safely predict its solubility in ethylene bromide to lie in the neighborhood of 0.15 mol per cent., in spite of the gloomy view of such a possibility implied by Kunerth.

The internal pressures of $CO_2$ and $N_2O$ are undoubtedly higher, and $N_2O$, the less polar and hence more regular in behavior, dissolves in chloroform to the extent given by Raoult's law, but less in ethylene bromide, which has a higher internal pressure; $CO_2$ being chemically more reactive and hence itself somewhat polar is less regular, but in all

[1] J. Chem. Soc., *117*, 1410 (1920).

the solvents listed dissolves to an extent whose order of magnitude at least is correctly indicated by Raoult's law, and falling off as expected with ethylene bromide and carbon bisulfide. The internal pressures of chlorine and phosgene can be shown to be about the same as that of carbon tetrachloride, so that solvents in this region of the table should be the best, dissolving these gases to the extent calculated by Raoult's law, as is indeed the case. The reader may judge for himself whether or not the data show that "the conclusion Hildebrand draws is very obviously not warranted."

In a paper by Mr. N. W. Taylor and myself, which is being submitted to the Journal of the American Chemical Society, the data of Kunerth are discussed from the standpoint of the polarity and chemical nature of the substances involved.

It may be objected that in ruling out polar substances the scope of the internal pressure theory is so restricted as to make it of little use. No one regrets more than I the very limited progress that has been made in the theory of solubility, and I am under no illusion of having solved the problem, but I insist that it is possible to make approximate predictions of solubility in a large number of cases, which is somewhat encouraging. I have deliberately sought to simplify the problem as much as possible by studying first the substances of low polarity, for I consider that the abnormal amount of attention that has been devoted to the most complicated of all solution, aqueous solution of electrolytes, results not from sound scientific method but from the abundant presence of water upon the earth. Having gained, as I believe, some insight into simple solutions, we should be able to make more progress in the study of the more complex, but not by the denial of the progress already made. The existence of discrepancies of a nature clearly recognized is no more serious in this case than it is with gaseous mixtures, where we use quite freely Dalton's law of additive pressures, although large numbers of gaseous mixtures do not obey it on account of chemical reactions between the components.

There are several further statements of Kunerth which call for comment. He says of the theory advanced by myself and others "it should follow from the point of view of this theory that . . . all substances which are completely miscible should have the same internal pressures." Now I have endeavored to make it clear that both experiment and theory indicate that very considerable differences in internal pressure and large deviations from Raoult's law are necessary before two liquid phases appear. In the paper by myself and Buehrer, which deals with such systems, we say that "but few of the substances in the table of internal pressures given in the third paper of this series are far enough apart in

internal pressure to form two liquid layers . . . . " The subject was also discussed in the first paper, pp. 1465–1468. Fig. 1 may serve to make this clear. The straight line $a$ on which $p$ is proportional to $N$ corresponds to Raoult's law. Increasing positive deviations of the usual type are illustrated by the curves $b$, $c$, $d$, and $e$. On $e$ there are three values of $N$ for a single value of $p$, the mixture separating into two liquid phases just as in the plot of the van der Waals equation we get three values of $V$ corresponding to the two phases, liquid and gas. In $d$ these have coalesced into a single point where the curve has a horizontal tangent and the mixture has a critical point. Curves $c$ and $b$ represent systems having but one liquid phase but deviating from Raoult's law, and having different internal pressures, like hexane and carbon tetrachloride, or different degrees of polarity, like ethyl alcohol and carbon bisulfide. The dictum of Kunerth quoted above is, therefore, untrue, and the difficulty which he says I recognize, p. 523, is his own, not mine.

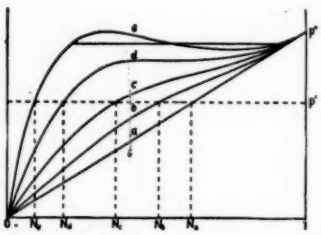


Fig. 1.

We can often produce the increasing deviations illustrated by $c$, $d$, $e$, by lowering the temperature, as with methyl alcohol and carbon bisulfide, or by replacing one component by another differing more from the fixed one in internal pressure or polarity. If the fixed component is under the vapor pressure $p'$ in a series of mixtures corresponding to the curves $a$ to $e$, its solubilities in these solutions will be $N_a$, $N_b$, $N_c$, etc. The possibility of two liquid phases appearing at higher pressures with $e$ does not set this system at all apart from the others when the lower pressure $p'$ is considered. Kunerth's distinction between completely miscible and incompletely miscible liquids, p. 520, seems therefore to be misleading.

The reader may be reminded, in conclusion, that a large amount of evidence is available as a test for theories of solubility in addition to the solubilities of gases discussed by Kunerth. The solubilities of solids can be calculated without the uncertainties present with gases due to violations of the gas laws, and various papers of our series present a large volume of such evidence. Evidence can be got further from critical mixing temperatures, and from the changes in boiling or freezing points produced by dissolved substances. This evidence must be considered as a whole, and that part derived only from one class of data cannot be singled out for refutation apart from the rest.

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October 26, 1922.

# THE VARIATION WITH FREQUENCY OF THE POWER LOSS IN DIELECTRICS.

By Hector J. MacLeod.

Abstract.

**Variation of the power loss in dielectrics with frequency, 500 to 1,000,000 cycles.**—(1) *A new bridge method of measurement* is described. This bridge has two resistance ratio arms, and two similar variable condenser arms which are made to act as pure capacities by connecting their dielectrics in parallel with the resistance arms. The condenser to be studied is connected in parallel with one of the bridge condensers set at zero. With this bridge the equivalent series resistance can be obtained directly without the assumption that the loss in the standard condenser is negligible. The theory of this bridge is given. For frequencies above 3,000 a resonance substitution method was used, correction being made for the losses in the standard precision condenser. (2) *Results for glass, Pyrex, paraffin, ceresin, mica and Murdock composition* are given. The power loss for unit voltage is equal to $2\pi fCF$, where $f$ is the frequency, $C$ the capacity and $F$ the power factor, which depends only on the material. Since the phase difference is small, $F$ is taken equal to $2\pi fCR$, where $R$ is the equivalent series resistance. It was found that, approximately, $R = A/f^k$, $P = Bf^n$; hence $F = D/f^{(k-n)}2$. For paraffin, mica, and Pyrex, the values found for $D$ are .00174, .0132, and .0264; the values of $(k - n)$ are .30, .23, and .215, respectively; and the values of $(n + k)$ are all close to 2, the difference being due to the small change of capacity with frequency. (3) *Relation to phenomenon of residual charge.* The constant $n$ is the same as in the equation of E. v. Schweidler for the residual charge current: $i = EC_0\beta t^{-n}$, where $E$ is the harmonic impressed electromotive force and $\beta$ is a constant. This equation leads to the above equation for power loss and also to the equation for the capacity: $C = C_0(1 + Mf^{n-1})$, where $M$ is a constant. Values of $n$ determined from the variation of capacity with frequency agree closely with those given above. This agreement both confirms the theory and indicates the accuracy of the measurements.

## Introduction.

In a perfect condenser the conductors or plates would have no resistance, the dielectric would show no absorption and its resistance would be infinite. In such a condenser the power loss would be zero and the current and impressed electromotive force 90° out of phase. Actual condensers only approximate to this ideal case, for the resistance of the conductors, though generally negligible, is never zero and the dielectric absorption is always accompanied by a loss of power which appears as heat in the condenser. This power loss signifies that there is a component of electromotive force in phase with the current. The effect of absorption is therefore equivalent to that of a resistance either in series or in parallel with the condenser.

The equivalent series circuit and vector diagram for a condenser with dielectric loss or conductor resistance is shown in Fig. 1. The resistance $r$ is called the equivalent series resistance. $\theta$ is the phase angle between the current and voltage and $\cos\theta$ is the power factor. The difference between 90° and the actual phase angle $\theta$ is called the phase difference $\psi$.

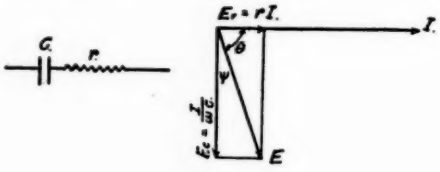


Fig. 1.

The power loss is given as for any part of a circuit by

$$P = EI\cos\theta = EI\sin\psi.$$

In all except extremely poor condensers, $\psi$ is very small. The angle $\psi$, its sine, and its tangent may, therefore, be taken as equal. When this is true, the power factor and phase difference are synonymous.

The power factor of a condenser may be determined by measuring the energy loss or the equivalent resistance. Since the energy loss is small it is difficult to obtain accurate results by the first method. However, by using the condenser as part of a resonance circuit, Rosa and Smith[1] were able to measure the loss by means of a wattmeter.

It is however less difficult to measure the equivalent resistance and this method has been used in a large number of experiments including those of Hanauer,[2] Monasch[3] and Lawther.[4] Lawther used a bridge method up to 1,360 cycles and a resonance method for higher frequencies. The ratio arms of the bridge were two similar condensers. The condenser to be investigated formed the third arm while the fourth contained a non-inductive resistance and an air condenser whose losses were considered negligible. He found that the series resistance $R$ may be represented by the equation $R = Af^k$ and the power loss by $P = Bf^n$ for condensers of glass and mica.

## Method and Apparatus.

Previous determinations of the energy losses in condensers have been made by comparison with an air condenser whose losses were considered negligible. In many cases, at least, this assumption has not been justi-

[1] E. B. Rosa and A. W. Smith, Phys. Rev., 8, 1899.
[2] J. Hanauer, Wid. Annalen, 65, 1898.
[3] B. Monasch, Ann. d. Physik, 22, 5, 1907.
[4] H. P. Lawther, Thesis, Harvard Univ. 1916.

fiable. In the present investigation, a bridge method was used for frequencies up to 3,000 and a special type of bridge was designed, which is believed to be new. The ratio arms are two equal fixed resistances and the other two arms of the bridge are variable condensers. The dielectric of the condensers is placed in parallel with the resistance arms and consequently the variable capacity arms of the bridge show no dielectric loss. Hence, neglecting the plate resistance, the capacity arms act as perfect condensers, assuming, of course, that air is a perfect dielectric.

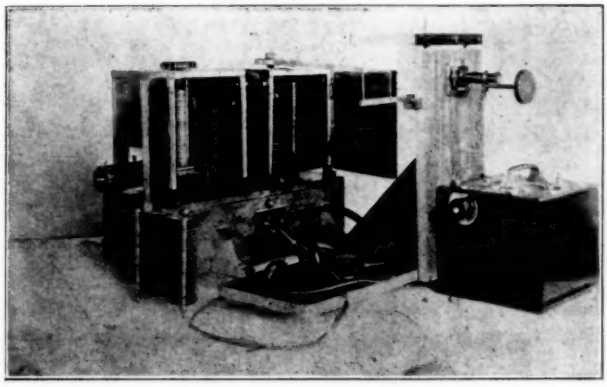

Fig. 2. The bridge.

Figure 2 is a photograph of the bridge. The diagram of connections is shown in Fig. 3 and the general arrangement of the four arms is illustrated by Fig. 4. The letters $A$, $B$, $C$, and $D$ indicate corresponding points in the two figures.

Referring to Fig. 3: The middle points of the primary and secondary windings of the input transformer are grounded. Since the resistance arms are equal, the point $D$ will remain at approximately earth potential. $A$ and $C$ will be high potential points and when the bridge is balanced, $B$ will remain at the same low potential as $D$.

Referring to Fig. 4: The copper lining and cover of the case containing the two resistance arms are connected to the point $D$. They are, therefore, at low potential. The high potential plate of the condenser $C_1$ above $A$ is supported by the block of hard rubber $E_1$ resting on the copper lining which is connected to the point $D$. This dielectric is therefore in parallel with the resistance $R_3$ between the points $A$ and $D$. The low potential plate of the same condenser and also the copper lining of its case are connected to the low potential point $B$. The condenser case is supported by four small blocks of hard rubber, which are fastened to the case of resistance arms. When the bridge is balanced, these two cases are at the

same low potential, consequently there is no loss in the hard rubber supports. The arrangement of the second condenser is similar in every way.

Special care was taken to have the bridge as symmetrical as possible. The blocks of hard rubber $E_1$ and $E_2$ (Fig. 4) were cut from the same piece. The condenser plates are separated by special 0.5 cm. spacers and the maximum capacity of each condenser is about 1,000 $\mu\mu$f. The ratio arms are made of equal resistances, each being approximately 11,500 ohms.

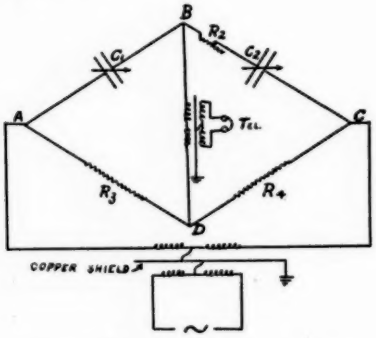


Fig. 3. Diagram of bridge circuit.

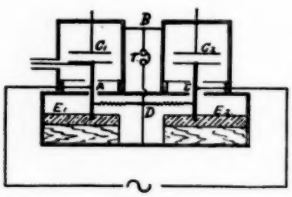


Fig. 4. Arrangement of bridge arms.

A balance in the bridge is indicated by means of a set of Baldwin phones, which are connected to the points $B$ and $D$ (Fig. 3) through a transformer completely enclosed by a grounded copper shield. The telephone and input transformers are similar to those used in the General Radio Company's capacity bridge. Each is made up of two sections symmetrically wound on a small closed laminated iron core. The primary and secondary windings are separated by a grounded copper shield. The middle point of the secondary winding of the telephone transformer is grounded, while in the input transformer both middle points are grounded. Thus there is no actual ground within the bridge itself. The fine adjustment of the condenser necessary for balance is obtained by a 17-inch lever arm fastened to the shaft of the condenser $C_2$ and controlled at its outer end by a rack and pinion.

When the bridge is balanced, the condenser $C_1$ is reduced to its zero value and the condenser, whose loss is to be determined, is connected in parallel with it by means of the terminals indicated in Fig. 4. The high potential terminal is a brass rod connected to the supports of the high potential plates. It is surrounded by a cylinder connected to the lining of the case and forming the low potential terminal. There is no direct dielectric support between the terminals.

It is important to have the resistance $R_2$, by which the bridge is balanced, practically a pure resistance. For resistances above 1,000 ohms a special resistance box was built in which six 1,000-ohm coils were placed three inches apart. The coils not in use were entirely disconnected from the circuit by means of double-throw switches.

The inductive effect of these coils was determined at 1,000 cycles by the substitution method with an impedance bridge. The standard was a 1,000-ohm single loop, whose dimensions were known and whose inductance could be calculated. 1,000 ohms in the resistance box was found to be equivalent to 1,000 ohms pure resistance shunted by 2.7 $\mu.\mu.f.$, while five coils were equivalent to 5,000 ohms shunted by 4.7 $\mu.\mu.f.$ The effect of these values on the power factor and capacity was negligible.

The standard of capacity used was a carefully calibrated 1500 $\mu.\mu.f.$ variable precision condenser made by the General Radio Company. In comparison with ordinary condensers its loss is small.

## The Oscillator.

A diagram of connections of the source of oscillations is shown in Fig. 5. It is a well-known arrangement and need not be described in

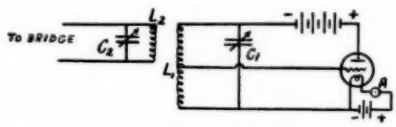


Fig. 5. Diagram of oscillator circuit.

detail. Resonance was obtained in the secondary circuit by means of the decade mica condenser $C_2$. The circuits were coupled as loosely as possible. The resonance e.m.f. impressed on the bridge was about 90 volts.

### *The Resonance Circuit.*

At high frequencies the ordinary resonance substitution method was used but the losses in the precision condenser had previously been determined at low frequencies and could be taken into consideration. The double-pole double-throw switch, by which either condenser could be thrown into the circuit, was made of paraffin containing small holes filled with mercury. For frequencies above 100,000 a Leeds and Northrup galvanometer, having a resistance of 7.23 ohms and a period of 1.8 seconds, was used with a thermocouple. For lower frequencies this instrument was replaced by a sensitive Weston Electric galvanometer.

## Theory of Bridge Circuit.

Let $z_1$, $z_2$, $z_3$ and $z_4$ represent the impedances of the corresponding arms of the bridge as indicated in Fig. 3.

$$z_1 = R_1 - J/\omega C_1, \qquad z_3 = R_3,$$
$$z_2 = R_2 - J/\omega C_2, \qquad z_4 = R_4.$$

The condition for zero current in the telephone circuit is that

$$z_1/z_2 = z_3/z_4$$

or, assuming an impressed sinusoidal electromotive force,

$$R_1/R_2 = C_2/C_1 = R_3/R_4.$$

$R_3 = R_4$ and therefore when the bridge is balanced $C_1 = C_2$ and $R_1 = R_2$.

Let $C_x$ be the capacity of the condenser to be investigated and $R_x$ its equivalent series resistance. This condenser is connected in parallel with $C_1$. Then by neglecting $R_x^2$ in the expression

$$R_x^2 + \frac{(C_x + C_1)^2}{C_x^2\, C_1^2 \omega^2}$$

it may easily be shown that

$$R_0 = \frac{R_x C_x^2}{(C_x + C_1)^2} \tag{1}$$

and

$$C_0 = (C_x + C_1), \tag{2}$$

where $R_0$ is the equivalent series resistance of this parallel circuit and $C_0$ its series capacity. In the condensers studied, $R_x$ was of the order of 1,000 ohms at 1,000 cycles, $C_x$ was 900 $\mu\mu$f. and $C_1$, 30 $\mu\mu$f. $R_x^2$ is, therefore, of the order of one millionth of the expression in which it has been neglected.

From equation (1)

$$R_x = \frac{R_0\,(C_x + C_1)^2}{C_x^2}. \tag{3}$$

This equation shows that it is desirable to have the capacity $C_1$ as small as possible in order that $R_0$, which is measured by the bridge, may be nearly as large as $R_x$, the equivalent series resistance of the condenser under investigation. Consequently the high potential plates of the condenser $C_1$ were made detachable and when removed the capacity of the terminals and supports alone remains. This capacity $C_1$ amounts to 32 $\mu\mu$f. Taking $C_x$ as 900 $\mu\mu$f., the correction factor in equation (3), viz., $(C_x + C_1)^2/C_x^2$, is 1.072.

## PROCEDURE.

These experiments were carried out in a constant temperature room of Cruft High Tension Laboratory. The oscillator was not in the same room as the bridge and resonance circuit. The capacity and equivalent series resistance of the condensers were determined by the bridge for frequencies from 500 to 3,000. The procedure was as follows: The condenser $C_x$ was connected to the bridge in parallel with $C_1$ which was set at its minimum value. The bridge was roughly balanced and the secondary circuit tuned to resonance. The frequency was then determined and an exact balance obtained in the bridge by adjusting the capacity $C_2$ and the resistance $R_2$ to the point of silence in the phones. The capacity $C_x$ was obtained by direct substitution of the Precision Condenser. The condensers $C_1$ and $C_2$ of the bridge were then made equal and the bridge itself was balanced. A few ohms were generally required for a perfect balance and they were added to or subtracted from $R_2$ obtained above. The result, substituted for $R_0$ in equation (3), gave the equivalent series resistance $R_x$ of the condenser under investigation. A series of values was obtained in a similar way covering the range from 500 to 3,000 cycles.

For the high frequency values the secondary circuit was resonated with the resistance set at zero and the condenser $C_x$ in the circuit. The coupling was then adjusted to nearly full scale deflection of the galvanometer. After carefully resonating and noting the deflection, the double-throw switch was thrown over to include the precision condenser in place of the condenser $C_x$. Resonance was again obtained by varying the precision condenser, and the required deflection by varying the resistance. The resistance introduced represents the difference between the equivalent series resistances of the two condensers. The effect of this resistance upon the capacity of the circuit becomes important at high frequencies. The equivalent capacity was, therefore, obtained by resonating the circuit by means of the precision condenser with the resistance box at zero. After each set of readings, the value of the resonance current with the condenser $C_x$ was checked to ensure that it had remained steady.

## SOURCES OF ERROR AND ACCURACY.

The sources of error in the bridge itself may be classified as follows:

(*a*) Errors in the ratio of $R_3$ and $R_4$.
(*b*) Inductance or capacity of the ratio arms $R_3$ and $R_4$.
(*c*) Inductance or capacity of the balancing resistance $R_2$.
(*d*) Electrostatic capacity between the bridge and its surroundings.

The error in the ratio of $R_3$ and $R_4$ can be made extremely small, especially when these resistances are large. Before the condensers were added to the bridge, the equality of the ratio arms was checked by balancing and interchanging two variable air condensers.

If the balancing resistance $R_2$ were a pure resistance, its introduction into the bridge arm would cause a change in the power factor of approximately $R_2\omega C_2$. When $R_2$ is equivalent to a pure resistance shunted by a capacity $k_2$, the change in power factor becomes $R_2\omega C_2[1 - (R_2\omega k_2)^2]$. As stated above, the value of $k$ for 5,000 ohms was found to be 4.7 $\mu.\mu.f.$ This represents a decrease in the power factor of about .0002 per cent. at 1,000 cycles.

The effects of the inductance or capacity of the ratio arms and of the electrostatic capacity of the bridge may be practically eliminated by the substitution method. These effects will enter into the measurements of the two condensers in the same manner since they are both measured in the same arm of the bridge. And if the capacities are equal, the errors will be sensibly the same and will not affect measurements of capacity or resistance.

The theory of the bridge circuit given above applies only in the case of a sinusoidal electromotive force and current. Harmonics generally occur in an audion circuit and in order to minimize their effect, the loose coupling and resonance previously described was used. Especially above 1,000 cycles, a sharp balance and silence in the phones was obtained and at high frequencies the resonance peak was extremely sharp. The effect of harmonics was, therefore, considered unimportant.

In order to ensure that the input transformer did not affect the observations, a set of readings was taken with and without this transformer in the circuit. These readings were consistent and showed no effect of the removal of the transformer. Without it, however, the value of the resistance required to balance the bridge itself was generally very much larger.

For the high frequency measurements, the two condensers were symmetrically placed with respect to the rest of the resonance circuit and the observations were checked with the condensers interchanged. The resistance, capacity and inductance of the circuit were varied by means of lever arms, which were also used with the bridge since the presence of the hand near it affected the balance.

It is well known that the equivalent resistance of condensers varies with the temperature. In the present investigation, the condensers were kept in the constant temperature room for at least several days before they were examined. After a series of observations had been

made, the results at about 1,000 cycles were checked in order to ensure that no change had taken place due to change in temperature or from any other cause.

The surface leakage of dielectrics exposed to air changes with the humidity. To minimize any possible surface leakage, nearly all the condensers studied were dried and dipped in molten paraffin or ceresin wax.

The percentage accuracy of the bridge measurements depended upon the equivalent series resistance of the condenser examined. Around 1,000 and 3,000 cycles, where the bridge was most sensitive, the resistance balance could be determined to the nearest half-ohm. Around 2,000 cycles, a balance to the nearest ohm could be obtained, while at frequencies below 800 or 900 the sensitivity was not so good. These values were practically independent of the equivalent resistance of the condenser. Since this resistance was obtained from the difference of two readings, the possible error above 1,000 cycles would be from .5 to 1 ohm. When the losses were above three or four hundred ohms, the observations were made to the nearest ohm only.

The capacity balance was much more sensitive than that of the resistance. The capacities of the condensers examined were about 900 $\mu.\mu.f.$ and a change in capacity of 0.2 $\mu.\mu.f.$ could easily be detected. This corresponds to about 0.02 per cent. A fine adjustment of the capacity was necessary in order to obtain the resistance balance.

The frequencies up to 3,000 were obtained by a frequency meter composed of a variable oil condenser and a set of inductance coils. The meter was calibrated with a set of tuning forks and checked on different occasions. Resonance was determined by a pair of phones connected to one terminal of the condenser. Over the range used, one division of the condenser scale changed the corresponding frequency by about 1 per cent. When a constant frequency was required for some time, a tuning fork was employed.

The high frequencies were determined by means of the Cruft wavemeter. The error in the frequency measurements throughout should not be more than about 1 per cent.

The measurement of equivalent resistance at high frequencies was probably most accurate around 250,000 cycles, where 0.1 ohm corresponded to about 8 or 10 small divisions on the galvanometer scale. Repeated observations agreed to within half a division.

## Tests of the Bridge.

The following tests of the bridge were made to ensure that the results obtained are reliable:

(*a*) To show that the addition of a condenser with no dielectric loss would not affect the balance of the bridge: A brass plate about 8 inches in diameter was fastened by a screw to the high potential terminal. This plate was surrounded by a firm brass case connected to the low potential terminal and supported on the table. The capacity of this condenser was about 600 $\mu.\mu.$f. The bridge condenser $C_1$ was reduced by the same amount and no change in the resistance balance was observed.

(*b*) To show that the equivalent resistance observed was approximately correct: The precision condenser and a resistance box were connected in series with the bridge terminals. The bridge was balanced with the resistance box at zero. A certain resistance was then included and the bridge again balanced. The following results are typical:

Capacity of added precision condenser: 900 $\mu.\mu.$f.

Resistance correction factor:

$$\frac{(900 + 32)^2}{900^2} = 1.072.$$

| $f$. | $B_1$. | $R_a$. | $B_2$. | $(B_2 - B_1) \times 1.072$. |
|---|---|---|---|---|
| 1,000 | 16 | 1,000 | 949 | 1,000 |
| 1,000 | 16 | 100 | 108.5 | 99.1 |
| 1,000 | 16 | 50 | 62.5 | 49.8 |
| 2,000 | 13 | 1,000 | 944 | 998 |

$f$ = frequency. $R_a$ = added resistance.
$B_1$ = balancing resistance when $R_a = 0$.
$B_2$ = balancing resistance with $R_a$ added.

By equation (3), $(B_2 - B_1) \times 1.072$ should equal the added resistance. This test also serves as a check on the accuracy of the correction factor.

(*c*) To show that correct results could be obtained with the bridge condenser at different settings: It is well known that equation (1), is applicable to an ordinary air condenser which may be considered as a variable pure capacity in parallel with a constant imperfect condenser. For a constant frequency, $R_x$ as well as $C_x$ is constant and the equation may, therefore, be written in the form:

$$R_0 = \frac{\text{const.}}{C^2}, \tag{4}$$

where $R_0$ is the equivalent series resistance of the condenser and $C$ its total capacity. Hence,

$$\log R_0 = \text{constant} - 2 \log C. \tag{5}$$

The results obtained for the variable precision condenser for a constant frequency of 1,024 cycles per second were as follows:

| Capacity ($\mu\mu$f.). | Resistance (Ohms). |
|---|---|
| 900 | 13 |
| 800 | 16 |
| 700 | 21 |
| 600 | 29 |
| 500 | 42 |
| 400 | 64 |
| 300 | 112.5 |

The graph of equation (5) for these results is a straight line with a slope of $-2$.

## Description of Condensers Examined.

*Glass No. 1.*—This was a commercial condenser made by the Wireless Specialty Apparatus Co. It consisted of copper coats electrolytically deposited on a glass jar. To reduce its capacity, the condenser was cut in two and the cylindrical part examined.

*Glass No. 2.*—This condenser consisted of a glass plate about 1/16 inch thick, which was sprayed with a metal coating after having been pitted by a sand blast. A heavy layer of copper was applied over a thin coat of lead. A one-inch margin was left all around. After the leads were attached, the condenser was dipped in paraffin.

*Pyrex.*—A thin-walled tube of pyrex was made in the form of a test-tube and supported inside another tube. After being carefully cleaned, the pyrex tube and the space between the tubes were filled with mercury to within about an inch and a half from the top.

*Paraffin.*—This condenser consisted of light copper plates separated by thin layers of paraffin. The condenser was also thickly coated over with paraffin.

*Ceresin.*—The high and low potential aluminum plates of a small air condenser were supported in a copper case. The case was filled with melted ceresin and allowed to cool in a vacuum. The supports were removed leaving the ceresin alone as the dielectric between the plates.

*Mica No. 1.*—This condenser consisted of a clear sheet of mica, the surface of which was slightly roughened and then sprayed with lead from an oxy-hydrogen gun. The condenser was padded with mica and clamped between brass plates. It was placed in a bath of melted ceresin under a bell jar. After the air had been exhausted, it was left to cool.

*Mica No. 2.*—A clear sheet of mica 5 cm. square was lightly coated with a rosin-beeswax mixture over which sheets of copper foil were pressed. The condenser was padded with sheets of mica and bakelite and clamped between heavy brass plates. It was then heated in an oven at about 100° C. and while still hot was clamped in a vise. After cooling, the clamping screws were again tightened and the condenser was coated with shellac.

*Composition No. 1.*—This was a commercial condenser manufactured by the W. J. Murdock Co. It consisted of copper sheets embedded in the composition. In order to reduce its capacity, the condenser was cut in two.

*Composition No. 2.*—This condenser was similar to Composition No. 1.

Glass No. 1, Mica No. 2 and Composition No. 2 were used by Lawther in experiments referred to in the introduction.

## Data and Curves.

In these experiments observations were made at about twenty different frequencies covering the range from 500 to 1,000,000 cycles. Only a few of these, however, are included in the following tables in which $f$ is the frequency in cycles per second; $R$, the equivalent series resistance of the condenser in ohms and $C$ its capacity in farads. P.F. represents the power factor.

Precision Condenser and Leads.
Capacity: 900 $\mu\mu$f.

| Observed. | | Obtained from Curve. | |
|---|---|---|---|
| $f$. | $R$. | $f$. | $R$. |
| 606 | 37.5 | 14,000 | 1.20 |
| 890 | 25 | 100,000 | .141 |
| 1,270 | 16.5 | 250,000 | .053 |
| 2,040 | 10 | 500,000 | .025 |
| 2,890 | 7 | 1,000,000 | .012 |

By plotting log $R$ against log $f$, a straight line was obtained. This line was produced and some of the high frequency values obtained from the curve are shown in the fourth column above.

*Glass No. 1.*

| $f$. | $R$. | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 498 | 1,383 | .9131 | .00395 |
| 1,015 | 634 | .9115 | .00368 |
| 2,820 | 203 | .9096 | .00327 |
| 14,000 | 34.2 | .9073 | .00276 |
| 100,000 | 4.14 | .9043 | .00236 |
| 500,000 | .75 | .9031 | .00213 |
| 1,000,000 | .35 | .9019 | .00198 |

Temperature: 20.8° C.

*Glass No. 2.*

| *f.* | *R.* | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 498 | 5,842 | .9222 | .0169 |
| 1,015 | 2,562 | .9149 | .0149 |
| 3,130 | 697 | .9052 | .0124 |
| 14,000 | 123.2 | .8977 | .00974 |
| 100,000 | 13.74 | .8875 | .00766 |
| 500,000 | 2.39 | .8803 | .00660 |
| 1,000,000 | 1.12 | .8773 | .00617 |

Temperature: 20.8° C.

*Pyrex.*

| *f.* | *R.* | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 596 | 4,281 | .8543 | .0137 |
| 1,010 | 2,354 | .8506 | .0127 |
| 2,920 | 719 | .8442 | .0111 |
| 14,000 | 120.2 | .8359 | .00884 |
| 100,000 | 14.3 | .8275 | .00743 |
| 500,000 | 2.58 | .8209 | .00666 |
| 750,000 | 1.76 | .8203 | .00678 |

Temperature: 20.4° C.

*Paraffin.*

| *f.* | *R.* | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 607 | 188.5 | .9124 | .000655 |
| 1,000 | 106 | .9122 | .000607 |
| 2,935 | 31.5 | .9118 | .000530 |
| 14,000 | 5.2 | .9115 | .000417 |
| 100,000 | .54 | .9121 | .000309 |
| 500,000 | .09 | .9115 | .000257 |

Temperature: 20.3° C.

*Mica No. 1.*

| *f.* | *R.* | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 590 | 1,947 | .9433 | .00680 |
| 1,020 | 988 | .9415 | .00595 |
| 2,890 | 303.5 | .9385 | .00516 |
| 14,000 | 51.9 | .9355 | .00427 |
| 100,000 | 6.1 | .9295 | .00356 |
| 500,000 | 1.12 | .9259 | .00326 |

Temperature: 20.3° C.

The data for Ceresin, Mica No. 2 and Composition No. 2 have been omitted. The two samples of mica were very similar and also the two samples of composition, while the results for ceresin are somewhat similar to those of paraffin.

*Composition No. 1.*

| *f.* | *R.* | $C \times 10^9$. | P.F. |
|---|---|---|---|
| 510 | 2,744 | .8881 | .00780 |
| 1,000 | 1,226 | .8840 | .00681 |
| 3,200 | 314 | .8815 | .00556 |
| 14,000 | 59.2 | .8791 | .00458 |
| 100,000 | 7.59 | .8746 | .00417 |
| 500,000 | 1.81 | .8716 | .00495 |
| 1,000,000 | 1.03 | .8713 | .00563 |

Temperature: 20.7° C.

## Discussion of Results.

In order to interpret the results obtained, the effect and probable importance of the different losses in condensers will first be considered. These losses are classified as follows:

(*a*) The leakage loss due to ordinary conduction through the dielectric or along its surface.

(*b*) The loss due to the phenomenon of dielectric absorption.

(*c*) The loss due to resistance in the metal plates or leads.

(*d*) The loss due to brush discharge which occurs only at high voltages and need not be considered here.

A condenser having leakage may be represented by a pure capacity with a constant resistance in parallel. The resulting phase difference $\psi$ is given by the equation: $\tan \psi = 1/R_p\omega C$.

This constant parallel resistance is equivalent to a series resistance $R_s$, which is equal to $1/R_p\omega^2C^2$ and hence decreases rapidly with increase of frequency. Previous experiments[1] have shown that with good dielectrics the leakage loss is small, being less than one per cent. of the total at a frequency as low as 50 cycles. Above 500 cycles, therefore, this loss may be entirely neglected.

The loss due to dielectric absorption is represented by an equivalent series resistance which decreases with increase of frequency. The resistance of the metal plates or leads is also a series resistance. The equivalent circuit of a condenser with dielectric loss or plate resistance is shown in Fig. 1. For this circuit, $\tan \psi = R\omega C$, which shows that the effect of a constant series resistance upon the power factor increases with the frequency. The resistance of the plates and leads is practically constant, although at high frequencies it may increase slightly on account of skin effect. In a well-designed condenser, this resistance is extremely small and is generally negligible in comparison with the equivalent resistance of the dielectric. At very high frequencies, however, it may become important.

[1] F. Tank (Ann. d. Physik, 48, 1915) and others.

In the present investigation, since the phase difference $\psi$ is small, $\sin \psi$ was taken equal to $\tan \psi$, giving the power factor P.F. $= \sin \psi = \tan \psi = R\omega C$, and for the power loss $P$: $P = \omega CE^2 \sin \psi = E^2 R\omega^2 C^2$. $R\omega^2 C^2$ therefore represents the power loss when the impressed voltage $E$ is equal to unity.

Curves were plotted in order to show the variation of the equivalent series resistance and the power loss with frequency. With the exception of the Composition condensers and Mica No. 2 above about 14,000 cycles, the log resistance-log frequency curves are apparently straight lines. When this is true,

$$\log R = \text{const.} - k \log f,$$

and

$$R = \frac{A}{f^k}, \tag{6}$$

where $A$ and $k$ are constants.

The values of $k$ are as follows:

| Condenser. | $k$. |
|---|---|
| Precision (and leads) | 1.08 |
| Glass No. 1 | 1.095 |
| Glass No. 2 | 1.13 |
| Pyrex | 1.10 |
| Paraffin | 1.15 |
| Ceresin | 1.13 |
| Mica No. 1 | 1.11 |
| Mica No. 2 | 1.39 |
| Composition No. 1 | 1.16 |
| Composition No. 2 | 1.18 |

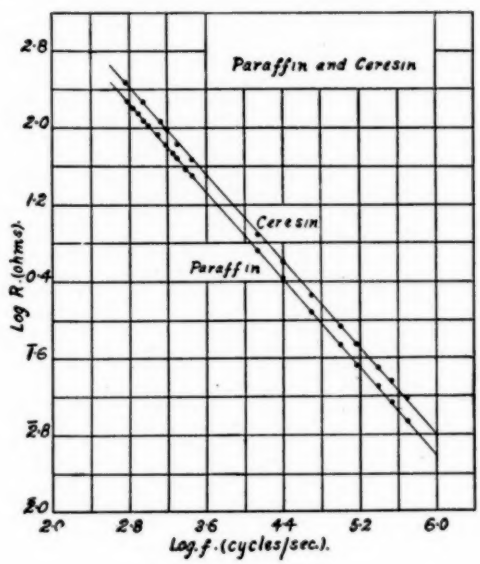


Fig. 6.

As previously explained, the values of $k$ for the precision condenser and leads were applied as corrections to all values of resistance obtained by the resonance method. A check on the accuracy of these corrections is given by the curve for the paraffin condenser which showed the smallest loss. Above 100,000 cycles the correction was over 22 per cent. of the total loss and yet the points lie well on the same straight line as the low frequency ones. The curves for paraffin and ceresin are shown in Fig. 6.

The deviation from a straight line at high frequencies in the case of the Composition condensers and Mica No. 2 represents a larger power loss. The composition was rather brittle and it is probable that the plates were loosened when the condensers were cut in two. While in the circuit, Composition No. 2 emitted a singing note throughout the audible range. For these condensers, which will be omitted from further discussion, the values of $k$ given above were obtained from the slope of the line below 14,000 cycles.

The log of the power loss for unit voltage, which is equal to $R\omega^2C^2$, is plotted against the log of the frequency in Figs. 7 and 8. These curves are also apparently straight lines and therefore

$$\log P = \text{const.} + n \log f$$

or

$$P = Bf^n. \tag{7}$$

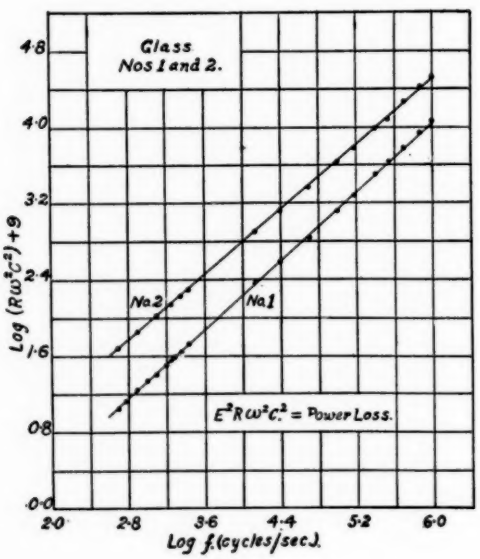


Fig. 7.

The values of $n$ are as follows:

| Condenser. | $n$. | $n + k$. |
|---|---|---|
| Glass No. 1 | 0.90 | 1.995 |
| Glass No. 2 | 0.86 | 1.99 |
| Pyrex | 0.885 | 1.985 |
| Paraffin | 0.85 | 2.0 |
| Ceresin | 0.86 | 1.99 |
| Mica No. 1 | 0.88 | 1.99 |

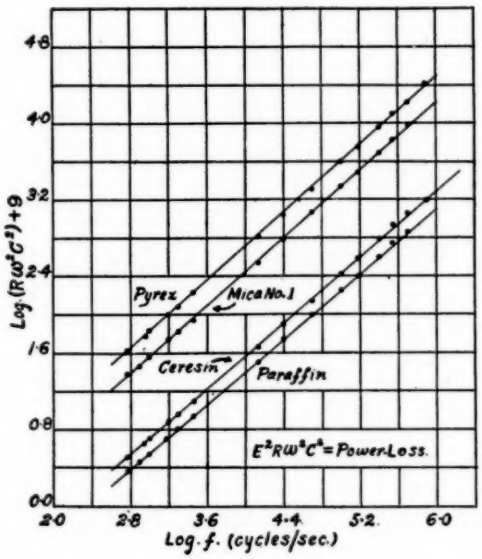


Fig. 8.

The sum of $n$ and $k$ is approximately equal to 2, the difference being due to the slight decrease in the capacity as the frequency is increased. This decrease and also the constant $n$ may be accounted for by the phenomenon of residual charge which has attracted the attention of many eminent physicists.

The experimental work of Kohlrausch,[1] E. v. Schweidler,[2] and others has shown that the residual charge current $i$ is given by the equation:

$$i = EC_0\beta t^{-n}. \tag{8}$$

$E$ represents the constant impressed electromotive force and $C_0$ the capacity for infinite frequency, which is sometimes called the geometrical capacity; $t$ is the time and $\beta$ and $n$ are constants. $n$ lies between zero and one.

[1] R. Kohlrausch, Pogg. Ann., 1854.

[2] E. v. Schweidler, Ann. d. Phys., 24, 1907.

E. v. Schweidler has shown that when

$$E = E_0 \sin \omega t,$$
$$i = \omega C_0 E_0 (G \cos \omega t + H \sin \omega t), \tag{9}$$

where

$$G = \omega^{n-1} \beta \Gamma(1 - n) \cos \frac{(1 - n)\pi}{2}$$

and

$$H = \omega^{n-1} \beta \frac{\pi}{2\Gamma(n) \cos \frac{(1 - n)\pi}{2}}.$$

$\Gamma(n)$ is the Gamma function.

The normal charging current $I_0$ is given by:

$$I_0 = \omega C_0 E_0 \cos \omega t \tag{10}$$

and the normal conduction current $j$ by

$$j = \frac{E_0}{W} \sin \omega t. \tag{11}$$

The total current $I$ is therefore:

$$I = \omega C_0 E_0 [(1 + G) \cos \omega t + \left( \frac{1}{\omega C_0 W} + H \right) \sin \omega t]. \tag{12}$$

Hence the apparent capacity $C$ is given by:

$$C = C_0 (1 + G) \tag{13}$$

and the power loss $P$ by:

$$P = 1/2 \, \omega C_0 E_0^2 \left( \frac{1}{\omega C_0 W} + H \right). \tag{14}$$

Substituting for $H$:

$$P = \omega C_0 E^2 \left( \frac{1}{\omega C_0 W} + \omega^{n-1} \beta \frac{\pi}{2\Gamma(n) \cos \frac{(1 - n)\pi}{2}} \right), \tag{15}$$

where $E$ is the effective voltage.

The first term in the brackets arises from the conduction or leakage current and the second term from the residual charge current or dielectric absorption. In the present investigation, the first is negligible in comparison with the second, and equation (15) reduces to

$$P = \text{const. } E^2 \omega^n.$$

For a constant voltage:

$$P = B f^n. \tag{16}$$

This equation is identical with equation (7) given above to represent the variation of power loss with frequency as shown by the curves. The exponent $n$ of the power loss equation is the $n$ which appears in the equation for the current due to residual charge. This was shown for a frequency of 50 cycles by the experiments of Tank[1] in which the constants $\beta$ and $n$ of the residual charge current equation were obtained for small values of the time $t$, by means of a Helmholtz pendulum.

Another method of determining $n$ is suggested by equation (13) which, on substituting for $G$, is:

$$\begin{aligned} C &= C_0\left[1 + \omega^{n-1}\beta\Gamma(1-n)\cos\frac{(1-n)\pi}{2}\right] \\ &= C_0(1 + \text{const. } \omega^{n-1}) \\ &= C_0\left(1 + \frac{M}{f^{1-n}}\right), \end{aligned} \tag{17}$$

where $M$ is a constant, and $f$ is not zero.
Hence

$$\log C = \log C_0 + \log\left(1 + \frac{M}{f^{n-1}}\right)$$

and

$$\Delta \log C = \Delta \log\left(1 + \frac{M}{f^{1-n}}\right). \tag{18}$$

By equation (18), the following values were found from the $\log C - \log f$ curve for Glass No. 2, using the points: $f$ = 1,000, 10,000 and 100,000:

$$n = 0.855, \qquad M = 0.182, \qquad C_0 = 857.0\ \mu\mu f.$$

So far as known, no values of $n$ determined by this method have been published. Between 1,000 and 100,000, the capacity change was 27.5 $\mu\mu f.$, which may be measured to within one per cent.

Equation (17) shows that this change is a function of $M$ as well as of $n$, and $M$ is proportional to $\beta$. No idea of the change in capacity can, therefore, be obtained from the value of $n$ alone and it is only when $M$ is fairly large that accurate values of $n$ can be obtained by this method. The same remark applied, of course, to the determination of $\beta$ and $n$ from the current due to residual charge. For example, neither method could be used with paraffin condensers in which there is practically no change in capacity with frequency.

The two values of $n$ obtained for Glass No. 2, viz.,

(1) From variation of power loss: $n = 0.86$,
(2) From variation of capacity: $n = 0.855$,

[1] *Loc. cit.*

are in good agreement. By substituting the first in equation (15) together with the value of $C_0$ obtained above, the constant $\beta$ was found to to be .0370. The value of the power loss $P$ was taken from the curve in Fig. 7. By substituting the second value of $n$ in equation (17), $\beta$ was found to be .0379. These values agree to within 2.5 per cent. and are important as a check on the accuracy of the power loss actually obtained.

The results of this investigation are, therefore, in agreement with the theory given above. They show that the power loss $P$ may be expressed by the equation: $P = Bf^n$ over the wide range of frequency used and there is apparently no reason why this equation should not hold at higher and lower frequencies. Although the actual losses may vary considerably, the value of $n$ does not. For instance, the loss in Glass No. 2 is twenty-four times as great as that in paraffin and yet the corresponding values of $n$ are 0.86 and 0.85, respectively. The condenser with the smaller loss may also have the larger value of $n$.

A comparison of the energy losses of various dielectrics may be conveniently made by means of their power factors, since the power factor is a function of the dielectric and does not vary with the capacity of the condenser. The power factors of the dielectrics studied are given in

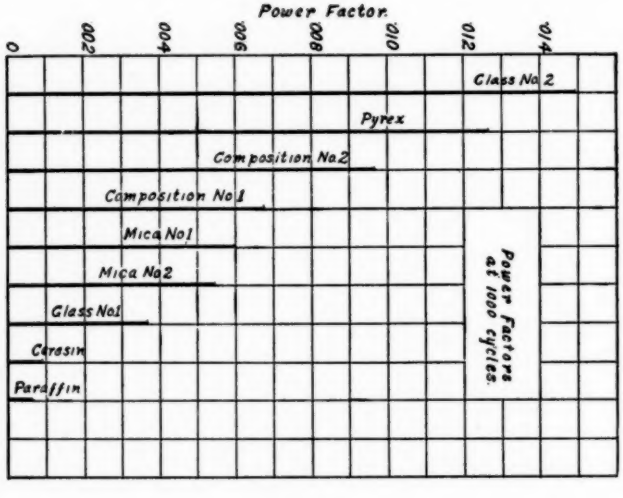


Fig. 9.

Fig. 9 for a frequency of 1,000 cycles. This figure shows clearly the comparatively small loss in paraffin and ceresin wax.

The power factor was taken as $R\omega C$, the tangent of the phase difference. It is greatest in glass No. 2 where the phase difference is about

51 minutes at 1000 cycles. The error caused by taking the tangent in place of the sine is less than .05 per cent.

From the equations for resistance and power loss, it follows that the power factor may be represented by the equation $P.F = D/f^{(k-n)/2}$, where $n$ and $k$ have the values given above and those of $D$ are as follows:

| *Condenser* | *D* |
|---|---|
| Glass No. 1 | .00714 |
| Glass No. 2 | .0373 |
| Pyrex | .0264 |
| Paraffin | .00174 |
| Ceresin | .00225 |
| Mica No. 1 | .0132 |

Since the $\log C - \log f$ curve is not exactly a straight line, the equation for the variation of the equivalent resistance, viz., $R = A/f^k$, is not absolutely consistent with the power loss equation. However, in the case of Glass No. 2 between 1,000 and 1,000,000 cycles, the deviation from the mean straight line is never more than about 0.22 per cent. It is considerably less in most of the other condensers. The effect of this deviation is well within the limits of experimental error and could not be observed on any of the resistance or power loss curves.[1]

The writer acknowledges with pleasure his indebtedness to Professor G. W. Pierce, under whose direction this work was carried out, for his interest, suggestions and criticism; also to Dr. E. L. Chaffee and Mr. R. F. Field for the frequent loan of special apparatus and for their assistance in other ways.

CRUFT LABORATORY,
HARVARD UNIVERSITY,
June 28, 1922.

[1] Note added January 30: It may be noticed, however, that there is a tendency for the points to lie slightly above the straight lines at high frequencies. This may be accounted for by the fact that the resistance of the plates and leads, though small and practically constant, is becoming of importance. By plotting the curves on a much larger scale, it was found that a small constant correction for points above 100,000 cycles brought them practically on the straight line.

# THE CHARACTERISTICS OF MAGNETICALLY ACTIVE IRON.

By Alva Turner.

Abstract.

**Permeability and hysteresis characteristics of annealed bessemer steel while magnetized with an alternating field (maximum intensity 0.25 to 4.5 gauss and frequency 30 to 103 cycles) for weak high frequency alternating fields 5,000 to 50,000 cycles.**—The method, suggested by Pupin, consisted in measuring, for the high frequency fields used, the effective inductance and resistance of coils wound on laminated steel cores, by means of an alternating current bridge connected in the circuit of the high frequency source which was synchronously interrupted except for 1/1,800 second at a known phase of the low frequency current. The permeability is proportional to the effective inductance, and the hysteresis loss was obtained by subtracting the copper resistance and calculated Foucault current resistance from the total resistance. Curves give the variation of permeability and hysteresis loss with phase of the low frequency field, for various intensities up to 4.5 gauss. They show maxima and minima for intensities above 0.25 gauss. On increasing the frequency of the high frequency field, the maximum permeability decreases and the maximum hysteresis loss increases. On increasing the frequency of the low frequency field, the maximum values of the permeability and hysteresis loss both increase.

WHEN two currents of different frequencies carried simultaneously by an electrical circuit produce a magnetic field in iron, investigation has shown that the hysteresis losses in the iron corresponding to one of the frequencies acting alone may differ greatly from those obtained for this frequency when the other is also present. The magnetic characteristics of the iron were studied for the high frequency alternating magnetizing force while the low frequency alternating magnetizing force was acting. The present investigation dealt with frequencies of from 30 to 103 cycles producing a magnetization of not more than 5 gauss, and frequencies of from 5,000 to 50,000 cycles producing a magnetization of not more than 0.01 gauss, acting simultaneously. These limits of range of the high and low frequencies were fixed by the apparatus.

## Summary of Previous Work.

In 1887 Lord Rayleigh[1] studied the effect of a constant magnetizing force on the susceptibility due to an alternating magnetizing force in iron. He found that as long as the constant force is moderately small, and the mean magnetization consequently not very strong, the susceptibility with regard to the alternating force is not materially different

[1] Ewing, Magnetic Induction in Iron, New Edition, page 127.

from the initial susceptibility of the same piece of iron when unmagnetized. However, as the mean magnetization is raised, the susceptibility with regard to the alternating force is reduced.

In 1917 Fritz Erhardt[1] published a paper on "Die Reversible Magnetische Permeabilitat bei Hohen Frequenzen." In this paper he considers the effect of a superposed moderately strong direct magnetizing force on the permeability of iron for a weak high frequency alternating magnetizing force at different frequencies. He found that the permeability for the alternating magnetizing force is independent of the frequency for frequencies up to 1,000,000 cycles per second.

In unpublished investigations dating back to about 1898 Prof. M. I. Pupin found that when a superposed alternating magnetizing force is substituted for the superposed constant magnetizing force of the preceding case the effect was quite different from that found by Lord Rayleigh. He recommended to me a further research of this problem and developed the experimental method employed.

In February, 1921, W. Fondiller and W. H. Martin[2] published a paper in which they dealt with the reaction in a telephone frequency circuit due to a superposed telegraph frequency circuit. Their problem is essentially different from the one under consideration here because it considers only that part of the cycle of superposed alternating magnetizing force which causes the largest disturbance in the telephone circuit, whereas this problem considers the effect of each part of the cycle of superposed alternating magnetizing force. An oscillograph in conjunction with an alternating current bridge was used in their experiment, whereas an interrupter in conjunction with an alternating current bridge was used in this experiment.

## Method of Procedure.

The two laminated cores, one of which is shown in Fig. 1, were made of plates 3 mils in thickness of ordinary annealed Bessemer steel which was obtained through Edgar Ward and Co. Two cores were used in order to reduce the disturbance in the bridge circuit due to the low frequency alternating force. On each of these cores were wound a primary and secondary winding of 4 coils each as shown in Fig. 2. The secondary windings were connected in series so that their magnetic field acted in opposition to that of the two primary windings also connected in series. The secondary winding was in the low frequency circuit.

An alternating current bridge was used to measure the effective resistance and inductance of the high frequency circuit. The circuit con-

[1] Annalen der Physik, 1917, page 41.

[2] Journal of A. I. E. E., page 149, February, 1921.

tained an ordinary decade bridge connected to a vacuum tube oscillation generator set through an interrupter. The interrupter is mounted on the shaft of a small motor which is run in synchronism with the low frequency

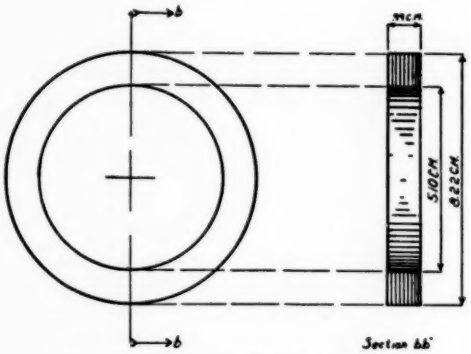


Fig. 1. Diagram of laminated iron core.

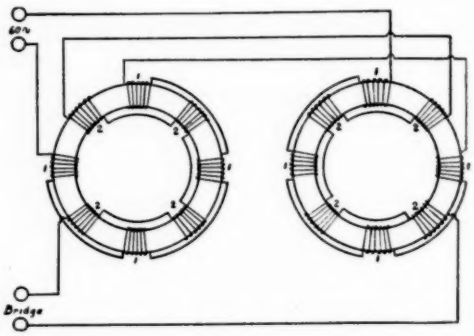


Fig. 2. Diagram of coils showing connections.

superposed alternating current. The time of each contact of the interrupter was 1/1,800 sec. Since the high frequency used ranged from 5,000 to 50,000 cycles per sec., each contact of the interrupter allowed from 3 to 30 cycles of the high frequency force to act simultaneously with any very small part of the low frequency cycle of the superposed alternating magnetizing force. As the motor made 30 r.p.s., causing the interrupter to make 120 contacts per sec., there were 120 pulses of from 3 to 30 cycles per pulse of the high frequency force present in the bridge circuit and thus in the secondary winding of the core each sec.

A detector, such as is commonly used in radio communication, was used to detect the note present when the bridge was unbalanced. When the interrupter makes contact it allows a series of high frequency cycles to pass into the bridge circuit as is represented by Fig. 3. The rectified portion of the current that enters the telephone is represented by Fig. 4.

Fig. 3. The interrupted high frequency current.

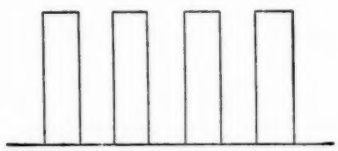

Fig. 4. Rectified portion of the interrupted high frequency current that enters the telephones.

This is a complex harmonic wave form and hence is present with all of its harmonics. Therefore the detector was tuned for the sixth harmonic

of this wave form as the ear and telephones are more sensitive for this higher frequency.

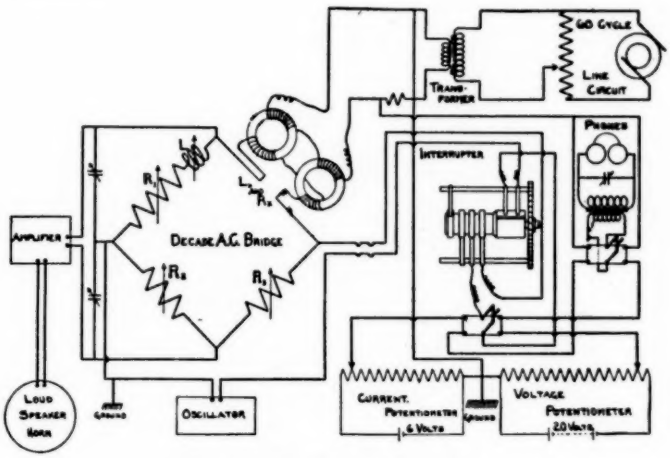


Fig. 5. Diagram of apparatus.

The intensity of the superposed low frequency strong alternating magnetizing force was made variable by means of a potentiometer arrangement in the low frequency circuit. Diagrams of the interrupter and circuits are found in Figs. 5 and 6.

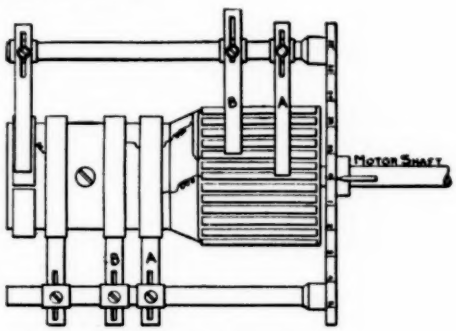


Fig. 6. Diagram of Interrupter.
*A*—Bridge Circuit, *B*—*E* and *I* circuits.

The resistance measured in the bridge arm is made up of three different components due respectively to energy losses produced by hysteresis, Foucault currents, and copper resistance. The component due to energy loss produced by hysteresis is obtained by subtracting the other two from the measured value. The copper resistance was measured in a direct current bridge and in this case could be assumed as sufficiently near to the same value for the highest frequency used. The resistance due to the energy loss produced by Foucault currents was found as follows:

The inductance measured in the bridge for imperfect penetration is expressed in terms of that for perfect penetration by the following formula:

$$L_1 = L_0 \frac{\sqrt{2\,(\cosh \alpha h - \cos \alpha h)}}{(\cosh \alpha h + \cos \alpha h)} \cdot \frac{}{\alpha h}$$

and the resistance due to Foucault currents is given by the following formula:

$$R_1 = L_0 \cdot \frac{\alpha^2}{2} \cdot \frac{1}{\alpha h} \cdot \frac{\sinh \alpha h - \sin \alpha h}{\cosh \alpha h + \cos \alpha h},$$

where $L_1$ = the effective inductance as measured by bridge.

$L_0$ = the effective inductance for perfect penetration. (The penetration is practically perfect for sample under test at 1,000 cycles per sec.)

$h$ = thickness of one plate of the laminated core.

$$\alpha = 2\pi \sqrt{\frac{f\mu}{\sigma}}.$$

$f$ = frequency, $\sigma$ = specific resistance of steel used.

$\mu$ = permeability which can be obtained from the following formula:

$$L_0 = 2S^2 n\mu h \log\left(\frac{b}{a}\right) . 10^{-9}$$

where $S$ = the number of turns of wire.

$n$ = the number of plates making up core.

$h$ = the thickness of one plate.

$b$ = larger or outer diameter.

$a$ = smaller or inner diameter.

Professor Pupin developed these formulæ mathematically and checked them experimentally. Using these formulæ the component of the effective resistance due to Foucault currents was calculated with a precision of only 1 per cent. since more accurate results were not warranted by the experimental data.

The high frequency was kept constant at 20,000 cycles per sec. and the low frequency at 60 cycles per sec., and the resistance and inductance curves per cycle of the low frequency superposed force were obtained for different values of intensity of this force varying from 0.28 to 4.5 gauss. The intensity of the high frequency alternating magnetizing force was less than 0.01 gauss and was kept constant throughout the entire experiment. These curves are shown in Fig. 7. This part of the ex-

periment was repeated for 5,000, 10,000, 30,000 and 50,000 cycles per sec. of the high frequency. The effect on the magnetic characteristics of the steel of changing the frequency of the high frequency alternating magnetizing force is shown in Fig. 10.

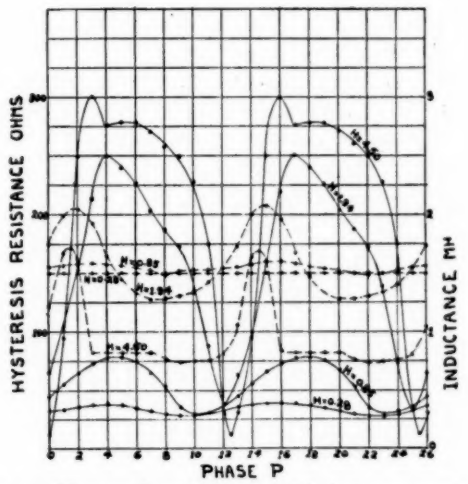


Fig. 7. Hysteresis resistance and inductance curves.

The curves of the impressed superposed alternating voltage and the alternating magnetizing force were obtained by the point-by-point method as described by Fitzhugh Townsend.[1] The circuit used to obtain these curves is shown in Fig. 5.

To show the effect of varying the frequency of the superposed alternating magnetizing force the intensity of this force was kept constant at 4.5 gauss, maximum value, and the frequency of the high frequency alternating magnetizing force at 20,000 cycles per sec. The frequency of the low frequency alternating magnetizing force was varied from 30 to 103 cycles per sec. (30, 60 and 103) and the maximum values of the hysteresis component of the effective resistance and effective inductance per cycle of this force were obtained for each frequency. The effect on the magnetic characteristics of the iron of changing the frequency of the low frequency superposed alternating magnetizing force is shown in Fig. 11.

The permeability is proportional to the inductance for a given frequency and therefore the inductance curve of Fig. 9 shows how the permeability changes throughout a cycle of the low frequency superposed alternating magnetizing force. The hysteresis loss for the high frequency can be calculated from the effective inductance, total effective resistance, and

[1] Transactions of A. I. E. E., January, 1900, page 5.

hysteresis component of the total effective resistance as follows: The mean effective value of the current, $I$, in the bridge circuit equals $E/(p^2L^2 + R_2^2)^{\frac{1}{2}}$ and the hysteresis loss, $I^2R$, equals $E^2R/(p^2L^2 + R_2^2)$, where $E$ is the mean effective value of the voltage across the secondary coil under test; $R$ is the hysteresis component of the effective resistance; $p$ equals $2\pi f$ where $f$ is the high frequency; $L$ is the effective value of the inductance and $R_2$ is the total effective resistance. Since $E$ is constant, $R/(p^2L^2 + R_2^2)$ was plotted in Fig. 9 in conjunction with the hysteresis loop as described in the following paragraph. This curve shows how the hysteresis loss changes throughout a cycle of the low frequency superposed alternating magnetizing force.

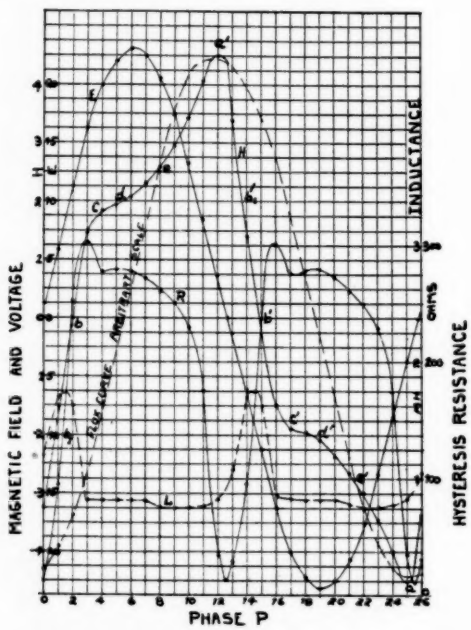


Fig. 8. Curves of impressed voltage, superposed force, hysteresis resistance and effective inductance. $E$, impressed voltage; $H$, superposed force; $R$, hysteresis resistance; $L$, effective inductance. $f$ = 20,000 cycles, $F$ = 60 cycles, $H$ = 4.5 gauss. 26 divisions of $P$ per cycle of 60-cycle force.

As a convenient means of studying the effect of a cycle of the low frequency superposed alternating magnetizing force on the permeability and hysteresis losses of the iron for the high frequency alternating magnetizing force, the values of these quantities were plotted in conjunction with the ordinary D.C. hysteresis loop for a cycle of this superposed force as is shown in Fig. 9. This hysteresis loop was obtained by the standard Ballistic Galvanometer method for values of $H$ over the same range as those of the $H$ curve of Fig. 8. This makes it possible to properly

plot the values of the hysteresis loss and inductance on the hysteresis loop of Fig. 9 in the following manner. On lines drawn from *O* to the several points of the loop magnitudes of hysteresis loss and inductance

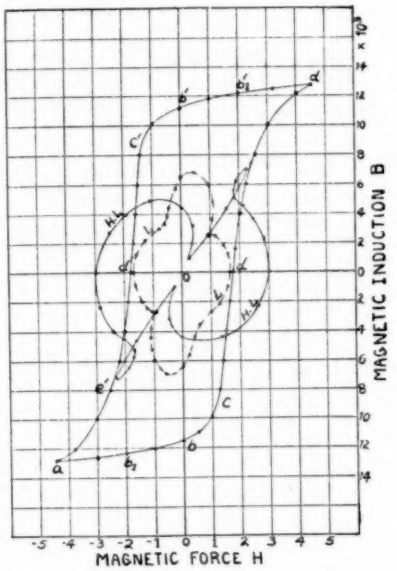


Fig. 9. Hysteresis loop for 60 cycles, inductance and hysteresis loss curves for 20,000 cycles. H.L., hysteresis loss curve; *L*, inductance curve. Scale for hysteresis loss and inductance curves, 2.5 div. = 1 millihenry, 2.5 div. = $2 \times 10^{-3} E^2$ watts. $H = 4.50$ gauss.

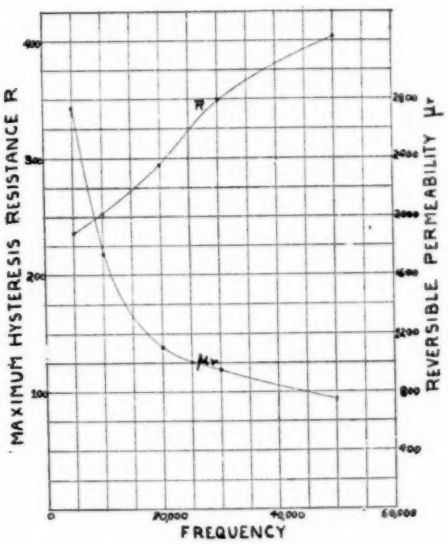


Fig. 10. Typical $R$ and $\mu_r$ curves. $H = 2.52$ gauss, $F = 60$ cycles. $\mu_r$ corresponds to the maximum inductance.

were laid off for the point on the hysteresis loop through which they are drawn.

The results of this investigation are correct to within 5 per cent.

## Conclusions.

The characteristics for the magnetically active iron are the same as those for this iron when it is not magnetically active, if the maximum intensity of the superposed alternating magnetizing force is 0.25 gauss or less; this is brought out by the curves of Fig. 7. For values of maximum intensity of this superposed force greater than 0.25 gauss the curves show a marked difference between the characteristics of magnetically active iron and those of this iron when it is not magnetically active. For a superposed force of 4.5 gauss, amplitude, the curves show that the effective inductance and the component of the effective resistance

due to hysteresis losses for 20,000 cycles are complex harmonic functions of the time with a fundamental frequency of 120 cycles per sec. when the superposed frequency is 60 cycles per sec. This indicates that the high frequency alternating current is modulated by the low frequency alternating current. The modulated high frequency alternating current was rectified and oscillograms were taken of this rectified current. These oscillograms of Fig. 12 show the complex harmonic rectified current with

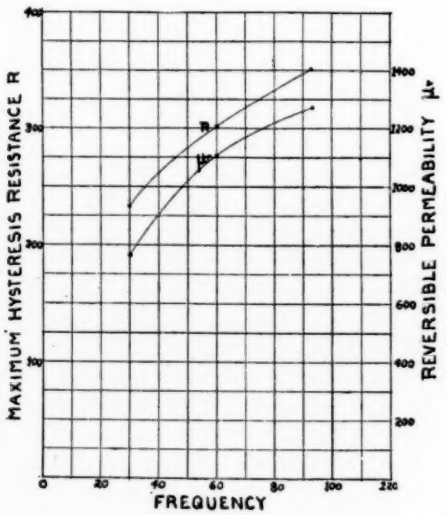


Fig. 11. Typical $R$ and $\mu_r$ curves. $H = 4.50$ gauss, $f = 20{,}000$ cycles. $\mu_r$ corresponds to the maximum inductance.

a fundamental frequency of 120 cycles per sec. in conjunction with the 60-cycle superposed alternating voltage for various circuit conditions.

The permeability for the high frequency alternating magnetizing force is a maximum for that part of the hysteresis loop where the magnetizing force is changing sign; this is the region $b$ and $b'$ of the curves of Figs. 8 and 9. The permeability changes rapidly from a maximum to a minimum during the part of the loop $bc$ and $b'c'$ of the Figures and is a minimum for that part of the loop where the flux is changing most rapidly and the superposed force is changing very slowly; this is the region $ce$ and $c'e'$ of these Figures. The hysteresis losses are a maximum for that part of the loop where the flux of the superposed force is approaching its maximum value, which is the region $ea'$ and $e'a$ of the Figures. These losses are large and practically constant for that part of the loop where the flux is changing most rapidly and the force is changing comparatively slowly; this is the region $ce$ and $c'e'$ of the Figures. These losses are a minimum for that part of the loop where the flux is a maxi-

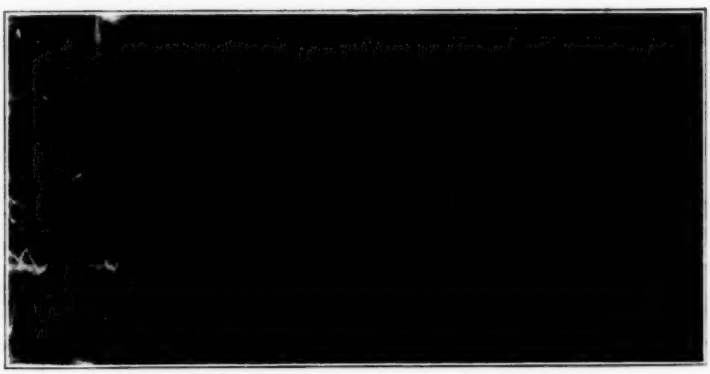

Fig. 12

ALVA TURNER.

mum and increase rapidly as the flux decreases from its maximum value; this is the region $ab$ and $a'b'$ of the Figures.

The maximum permeability, after correction is made for imperfect penetration, decreases and the maximum hysteresis component of the

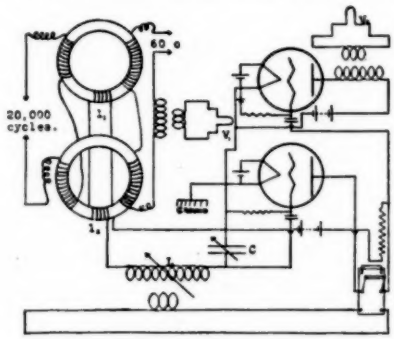


Fig. 13. Circuit to obtain oscillograms. $L$ is approx. $7(I_1 + I_2)$, $C = 1$ milli-microfarad. $V_1$ and $V_2$ are oscillograph vibrators. This was a distortionless circuit.

effective resistance increases as the frequency of the measuring current is increased. This is shown by the curves of Fig. 10. The corresponding values of permeability and resistance increase as the frequency of the superposed force is increased. This is shown by the curves of Fig. 11.

The writer wishes to express his obligations to Professor Pupin for frequent suggestions during the progress of this investigation.

MARCELLUS HARTLEY RESEARCH LABORATORY,
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August 10, 1922.

# THE SENSIBILITY OF THE EAR TO SMALL DIFFERENCES OF INTENSITY AND FREQUENCY.

By Vern O. Knudsen.

Abstract.

**Intensity and pitch sensibilities of the ear as functions of loudness and frequency.**—Intensity sensibility is defined, as usual, as the ratio of the least perceptible difference of energy to the total energy of that tone, $\Delta E/E$, while pitch sensibility is the ratio of the least perceptible difference of frequency to the frequency of the tone, $\Delta N/N$. There are considerable discrepancies among the results of previous investigators. The author used as a source of sound a telephone receiver actuated by a current from a vacuum tube oscillator. The intensity or the pitch could be changed periodically, once a second or so, by automatically changing the resistance or capacity in the oscillating circuit. The method of observation, then, was to change $\Delta E$ or $\Delta N$ continuously until the threshold of perception of fluctuation was reached. Separate observations usually checked within 10 per cent. As auxiliary experiments, in which the intensity was varied by changing the distance, showed that the acoustical energy of the source was a linear function of the electrical energy input, the latter was used as a convenient measure of the intensity of the sound. The frequency scale was determined by calibration. While the curves for the ears tested show individual differences, the results are in general the same for all. The intensity sensibility was found to be about 0.10 for moderate and high intensities but to increase to the limiting value 1 as the intensity decreases to the threshold. The curves are very similar to those obtained for the eye, and the *modification of the Weber-Fechner law* proposed by Nutting for light sensation also fits the results for audition satisfactorily: $\Delta E/E = F + (1 - F)(E_0/E)^n$, where $E_0$ is the threshold intensity and $F$ is about 0.10. The exponent $n$ varies somewhat with the frequency, being 1.65 for 200 d.v. and 1.05 for 1,000 d.v.; nevertheless at the same loudness level, for instance 10,000 $E_0$, $\Delta E/E$ is nearly independent of frequency, showing only a 10 per cent. variation from 100 to 3,200 d.v. The results were the same whether harmonics were present or not. It is concluded that for 1,000 d.v. under favorable circumstances the normal ear can distinguish about 400 gradations of loudness between the threshold and a painful intensity $10^{12}$ times as loud. The pitch sensibility, $\Delta N/N$, was found to depend on relative loudness in nearly the same way as $\Delta E/E$. For the same loudness level, $\Delta N/N$ decreased from 0.01 at 50 d.v. to 0.003 at 600 d.v. and then remained constant up to 3,200 d.v. The limit of perception of variation of pitch was about the same or trained as for other ears, but training helped in distinguishing which note was higher. Two ears were found more sensitive than one ear to small differences of pitch but not to small differences of loudness.

## I. Introduction.

We can arrive at a restricted arbitrary solution of the sensibility of the ear by determining the smallest perceptible increments of loudness, pitch, and quality for tones of all gradations of loudness, pitch ,

and quality. Thus the ratio of the smallest discernible difference of any arbitrary tonal stimulus to the whole stimulus will serve as a means of expressing the sensibility of the ear at that loudness, pitch, and quality. Hence if we can determine the ratios of the least discernible differences of loudness and pitch and quality of a tonal stimulus to the whole stimulus for tones of all gradations of these three properties, we should obtain a relative measure of how the sensibility of the ear depends upon these characteristic properties of sound. This leads us to the purpose of the present investigation, namely:

I. To determine how the sensibility of the ear to small differences of intensity varies with loudness and pitch. This "intensity sensibility" is expressed by the ratio of the smallest perceptible difference of the energy of a tone to the total energy of that tone, $\Delta E/E$.

II. To determine how the sensibility of the ear to small differences of frequency varies with loudness and pitch. This "pitch sensibility" is expressed by the ratio of the smallest perceptible difference of the frequency of a tone to the whole frequency of that tone, $\Delta N/N$.[1]

## II. Historical Survey.

### 1. *Sensibility of the Ear to Small Differences of the Intensity.*

The history of this phase of the sensibility of the ear begins with the Weber-Fechner law, which states that for each of our senses the increase of a stimulus necessary to produce a just discernible increase of sensation bears a constant ratio to the total stimulus. This constant ratio is called the Fechner constant.[2] In standard works on psychology, such as Wundt's, the value given to this ratio for the perception of sound intensity is one third.[3] This value is about the average of a number of early measurements obtained for noises produced by the impacts of balls against wood or metal plates, or by varying the distance from a ticking watch to the head of an observer.

Thus, in 1880, Fischer and Wundt[4] conducted a large number of experiments in which the smallest perceptible increment of sound intensity was determined by comparing the heights of fall of two similar lead balls which made successive impacts upon the fall-plate of a Hepp fall appa-

[1] This measure of sensibility has been employed by previous investigators and for that reason is used in this article. It is a little misleading since the smaller the values of $\Delta E/E$ and $\Delta N/N$ the greater the sensitivity of the ear. It would be better to use the inverse ratio or the logarithm of the inverse ratio to express these sensibilities.

[2] In the present paper we shall call this ratio the "Fechner ratio" and not the "Fechner constant," since, as we shall see, it is not a constant.

[3] Wundt's Human and Animal Psychology, p. 30. Wundt gives this same value to the Fechner ratio for the sensations of "warmth" and pressure.

[4] Wundt, Phil. Stud., p. 495.

ratus. By using balls of different weights and various heights of fall, they could produce various intensities of sound. Their results indicate that the Fechner ratio is independent of the intensity of the noise. They give for the value of the ratio .4055.

Max Wien[1] may be properly called the pioneer worker in determining the Fechner ratio for musical tones. Wien used as a source of tone a telephone receiver near the mouth of a Helmholtz resonator. He measured the intensity of the sound by optically projecting and amplifying the motion of a diaphragm placed within the resonator. A rubber tube connected the resonator to the observer's ears. Wien used chiefly the method of minimal change. His average values of $\Delta E/E$ for the three tones with which he worked are:

| Pitch | $a$(220 d.v.) | $e^1$(337 d.v.) | $a^1$(440 d.v.) |
|---|---|---|---|
| $\Delta E/E$ | .224 | .176 | .131 |

He therefore concludes that $\Delta E/E$ is a function of the frequency and uses the above data to determine the relative sensibility of the ear at the three different frequencies. His value of $\Delta E/E$ also varies with the intensity, increasing in general for very feeble and very loud tones, but rather irregularly.

A. Deenik[2] working with tuning forks and organ pipes records the following values:

(*a*) With Tuning Forks,

| Pitch | $c^1$(256 d.v.) | $c^2$(512 d.v.) | $c^3$(1024 d.v.) |
|---|---|---|---|
| $\Delta E/E$ | .332 | .295 | .195 |

(*b*) With Organ Pipes,

| Pitch | $C$ | $c$ | $c_1$ | $c_2$ | $g_2$ | $c_3$ | $g_3$ | $c_4$ | $c_5$ | $c_6$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta E/E$ | .232 | .218 | .163 | .131 | .105 | .125 | .112 | .085 | .107 | .192 |

### 2. *Sensibility of the Ear to Small Differences of Frequency.*

Vance[3] has given a good historical survey of the problem of the smallest perceptible difference of pitch and has also contributed valuable data to the subject. One has only to examine the existing data on the pitch-discriminating power of the ear given by Preyer,[4] Luft,[5] Meyer,[6] Stucker,[7]

[1] Über die Messung der Tonstärke; Max Wien, Wied. Ann. der Phys., 36, 834 (1888).

[2] Über das Unterschiedungsvermögen fur Tonintensitaten. A. Deenik, Versl. K. Ak. van Wet. afd. Natuutk., 14, 396.

[3] Variation in Pitch Discrimination Within the Tonal Range, T. F. Vance, Psychol. Monograph, No. 69, 16, p. 115. See also Nagel's Physiologie des Menchen, 3, p. 483.

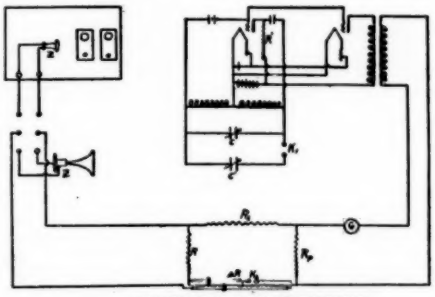
[4] Über die Unterschiedsempfindlichkeit fur Tonhöhen, W. Preyer, Jena, 1876, p. 24.

[5] Die Unterschiedsempfindlichkeit fur Tonhöhen, E. Luft, Phil. Stud., 4, *511* (1888).

and Vance[8] to learn that there are notable discrepancies among the results of these principal investigators.

## III. Apparatus and Method.

1. *Apparatus.*—Fig. 1 shows a schematic circuit diagram of the essential features of the apparatus used for the experiments described in this paper. The source of sound used is a telephone receiver actuated by energy from a vacuum tube oscillator. The oscillator can produce in the receiver tones of any desired frequency between 30 d.v. and 20,000 d.v. By means of a divided and balanced resistance circuit in the output of the oscillator the intensity of the tones can be varied by any desirable and measurable intervals from barely audible tones up to tones sufficiently loud to excite the sensation of pain. The wave form of the oscillator current is maintained practically sinusoidal by making $R'$, the plate resistance in the oscillating tube, sufficiently large to limit the amplitude of the oscillations to the extent that the tube amplifies linearly. In many of the tests the possible error from overtones was further eliminated by associating the receiver with appropriate resonators.



SCHEMATIC CIRCUIT DIAGRAM

Fig. 1.

The circuit is so designed that a motor-controlled key periodically changes, by any desired intervals, the resistance $R$ across which the receiver is shunted. The tone emitted by the receiver will therefore periodically and abruptly fluctuate from a tone of one intensity to a tone of greater or lesser intensity. The duration of each tone and the rate of fluctuation are easily controlled—the former by the amount of mercury in a cup into which the tongue of the key dips, the latter by the

[6] Über die Unterschiedsempfindlichkeit fur Tonhöhen, M. Meyer, Zsch. Psy. u. Physiol. d. Sinn., *16*, 352 (1889).

[7] Über die Unterschiedsempfindlichkeit fur Tonhöhen in Verschiedenen Tonregionen, N. Stücker, Setz. d. & ath. Kl. d. Kaiserl. Ak. d. Wiss., Wien, 1907, 116, 367.

[8] Loc. cit.

speed of the motor which operates the key. For best working conditions the two tones are of equal duration and alternate at a rate of about 50 per minute. This period is often changed and interrupted, and sometimes the key is operated manually, in order to eliminate the possibility of the observer possessing any after image or persistence of the rhythm of the changes after his liminal difference has been reached.

The means employed for changing the frequency is as simple as that used for changing the intensity. The same motor-controlled key is used to successively open and close $K_1$. This periodically increases the capacitance of the oscillator circuit by an amount $c'$. $c'$ is made up of a combined glass and air variable condenser whose capacitance can be varied continuously from zero upwards. The frequency of the tone emitted by the receiver will therefore alternately wax and wane by an amount which is determined by the values of $c$ and $c'$.

2. *Method of Making Measurements.*—The procedure for determining the smallest perceptible difference of intensity is as follows: The observer holds the receiver snugly to his ear, or, when the resonator is used as the source of the tone, he holds to his ear a rubber tube which is connected to the resonator. The resistance $R$ and $\Delta R$ (Fig. 1) are adjusted to such values that when $K_2$ is opened or closed (either manually or by the motor control) the difference of intensity of the two emitted tones is plainly perceptible. Then $\Delta R$, a portion of a slide wire resistance, which is added to $R$ when $K_2$ is closed, is gradually decreased until the observer no longer recognizes a difference of intensity. The observer signals his judgments to the operator by means of two signal lamps. The judgment of the disappearance of the difference of intensity of the tones is a rather simple judgment since it consists of deciding when a flutter tone merges into a steady tone. Then a second judgment is made to determine when the difference is just barely perceptible as the difference of intensity is increased from a non-perceptible amount; that is, $\Delta R$ is increased from zero until the observer recognizes the first appearance of the flutter. With a little practice and careful attention one can easily reproduce decisions of appearance or disappearance of the flutter within limits of about 10 per cent. A number of observations, four or more, are taken for each tone and the average of these is used to compute the Fechner ratio $\Delta E/E$. The method of this computation depends upon a linear relation between the electrical energy which actuates the receiver and the acoustical energy developed by the vibrating diaphragm.

3. *Relation between the Acoustical and Electrical Energies in a Telephone Receiver.*—The following experiments indicate a linear relation between the acoustical and electrical energies in a telephone receiver. The ex-

periments were performed over the campus lawn away from reflecting surfaces and where, as Wien has shown,[1] the intensity of sound radiation obeys the inverse square law. A telephone receiver, actuated by the vacuum tube oscillator already described, was supported overhead by a pulley, cord, and reel arrangement so that the receiver could be suspended at any distance, up to 10 meters, above the head of the observer. The current in the receiver could be adjusted by the attenuating circuit in the output of the oscillator.

In one experiment the telephone receiver was adjusted to such a distance above the ears of the observer that the tone just ceased to be audible. Then the distance from the ears to the receiver was altered and the receiver current adjusted until the threshold intensity was again obtained. Curve I., in Fig. 2, shows the relation between the current in the receiver, $I_R$, and the distance from the ears of the observer to the receiver to produce the threshold intensity for a tone whose frequency was 700 d.v. Similar curves were obtained for tones of 250 d.v. and 2,000 d.v. Since the presence of noise seriously interferes with the accuracy of locating the threshold intensity, these data were taken during the summer recess, 1921, and most of the observations were made at night under conditions particularly free from disturbing noises.

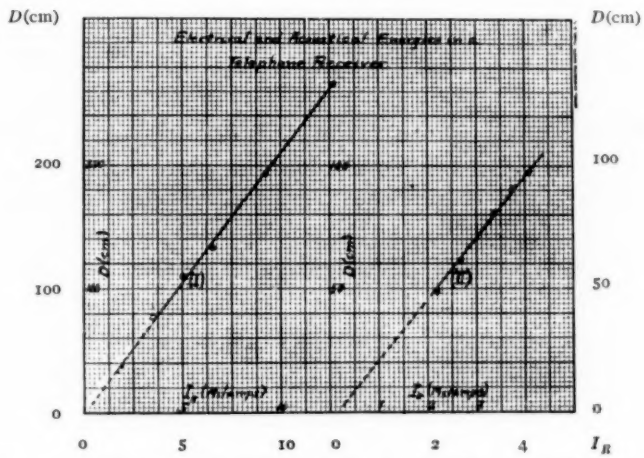



Fig. 2. Electrical and Acoustical Energies in a Telephone Receiver

In a second experiment the tone in a movable receiver was compared and made equal in intensity to the intensity of a tone in a receiver maintained at a constant distance above the observer's ears and actuated by a constant current of the same frequency as the current in the movable

[1] Loc. cit.

receiver. Ten separate judgments were averaged for each comparison, five with the compared tone just louder than the standard tone and five with the compared tone just feebler than the standard tone. Curve II, Fig. 2, shows the relation between the distance from the movable receiver to the observer's ears and the current required in the movable receiver to produce in it a tone of the same intensity as that of the constant standard tone in the fixed receiver. The frequency of the tone for Curve II was 700 d.v. Similar curves were obtained for tones of 250 d.v. and 2,000 d.v.

Assuming the inverse square law, the linear character of Curves I and II shows that for a wide range of receiver currents the acoustical energy developed by the vibrating diaphragm is a linear function of the electrical energy which actuates the receiver. For any fixed frequency, therefore, the electrical energy in the receiver is a convenient and reliable relative measure of the acoustical energy developed by the receiver diaphragm.

The change of the current in the receiver can therefore be used as a measure of the smallest perceptible difference of intensity of musical tones. Thus the ratio of the smallest discernible change of amplitude of a tone to the total amplitude will be given by the ratio of the change of current in the receiver to the total current. This latter ratio is conveniently computed from a simple equation which we shall now derive.

4. *Equation for Computing the Fechner Ratio* $\Delta E/E$.—The attenuating and measuring circuit by which the current in the receiver can be controlled and computed is shown in Fig. 1. $R$, $R_s$, and $R_p$, are non-inductive resistances. $R$ is a rather low resistance, about 20 ohms or less. $\Delta R$ is usually of the order of one ohm and is added to $R$ when $K_2$ is open. $R_s$—divided and distributed in two equal parts to keep the line balanced—is large, 5,000 ohms. $R_p$ may have any value between zero and infinity. $Z$, the impedance of the receiver when held against the ear, varies from 105 ohms at 100 d.v. to 2,080 ohms at 9,000 d.v. $G$ is a Duddell Thermo Galvanometer which measures the current $I$ flowing into the attenuating network.

With $K_2$ closed the current in the receiver, $I_R$, is

$$I_R = \frac{R_p R I}{\left(R_p + R_s + \frac{RZ}{R+Z}\right)(R+Z)}. \qquad (1)$$

With $K_2$ open $R$ is given the increment $\Delta R$ and $I_R$ is given the increment $\Delta I_R$. Since $R$ and $\Delta R$ are small compared with $R_s$, $I$ will not be

sensibly changed. Therefore,

$$I_R + \Delta I_R = \frac{R_p(R + \Delta R)I}{\left(R + R_s + \frac{(R + \Delta R)Z}{R + \Delta R + Z}\right)(R + \Delta R + Z)}. \quad (2)$$

Hence,

$$\frac{\Delta I_R}{I_R + \Delta I_R} = \frac{\Delta RZ}{(Z + R)(R + \Delta R)}. \quad (3)$$

Equation (3) therefore gives the ratio of the smallest perceptible increment of the amplitude of vibration of the tone to the total amplitude. Then the Fechner ratio, that is, the ratio of the smallest perceptible increment of energy of the tone to the total energy of the tone, $\Delta E/E$, is given by

$$\frac{\Delta E}{E} = \left(1 + \frac{\Delta I_R}{I_R + \Delta I_R}\right)^2 - 1. \quad (4)$$

5. *Method for Determining* $\Delta N/N$.—In paragraph 2 was described the procedure for making measurements on the smallest perceptible difference of loudness. The same procedure is followed for making measurements on the smallest perceptible difference of pitch, except that the frequency instead of the intensity of the tone emitted by the receiver alternately waxes and wanes. The $\Delta N/N$ could be determined from the average value of $c'$, $c$, and the equation for the frequency of the oscillator; but since the latter is rather complicated it is simpler and more accurate to calibrate the frequency of the oscillator experimentally for small changes of $c$. This was done by comparing the frequency of the oscillator with the frequency of standard König tuning forks which were maintained at a constant temperature. By counting the number of beats for slightly different values of $c$ the rate of change of frequency for small changes of c, $\Delta N/\Delta c$, was determined for tones covering the entire range of pitch from 50 d.v. to 4,800 d.v. From these values of $\Delta N/\Delta c$, curves were prepared from which one can read directly the percentage change of frequency corresponding to any possible change of $c$.

## IV. Experimental Results.

1. *Sensibility to Small Differences of Intensity as a Function of Loudness.*—Fig. 3 shows how the sensibility of the ear to small differences of intensity depends upon the loudness of sound. The curves show the relation between the Fechner ratio, $\Delta E/E$, and the relative amplitude of vibration of tones of 400 d.v., 1,000 d.v., 2,000 d.v., and 4,000 d.v. The relative amplitude of vibration of the tones is expressed by the ratio of the current

in the receiver, $I_R$, to the current in the receiver, $I_0$, required to produce the threshold intensity. Each curve shown is an average of four separate curves taken on different days. Each point on the separate curves, not shown in the figure, is the average of six independent judgments. Therefore each point indicated on the curves in the figure is an average of 24 separate judgments.

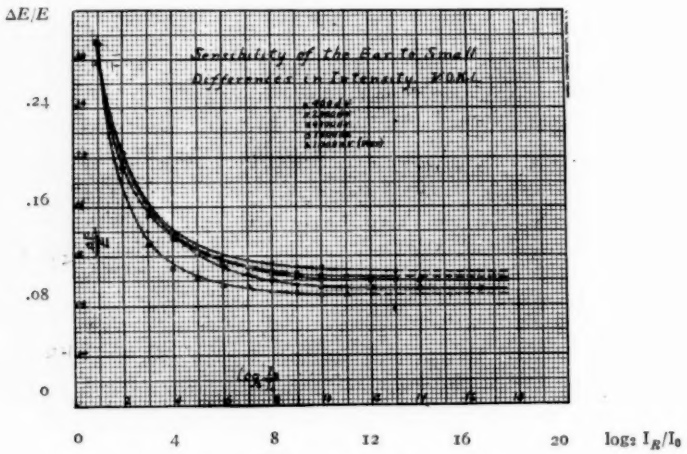



Fig. 3. Intensity Sensibility of the Ear

All but one of the curves in Fig. 3 are for the writer's left ear. Similar curves were obtained for the ears of three other persons, one of which is the lowest curve in Fig. 3. None of the other curves differed appreciably from those shown. The character of all of these curves shows that the sensibility of the ear to small differences of intensity is some continuous function of the intensity, but not as simple as the Weber-Fechner law requires. For feeble intensities the Fechner ratio is almost inversely proportional to some logarithmic function of the intensity. For moderate and high intensities the ratio is nearly constant, and hence for moderate and loud tones the original form of the Weber-Fechner law is quite valid. The value of the ratio, however, at least for musical tones, is not one third but more nearly one tenth.

From the values of the smallest perceptible difference of intensity shown by the curve for 1,000 d.v., it follows that the normal ear, under the most favorable conditions, can distinguish about 400 gradations of loudness between the limits of intensity to which the ear responds. The energy of the loudest audible tone at 1,000 d.v., that is, the energy of a tone which is sufficiently loud to just excite the sensation of pain, is about $10^{12}$ times as great as the energy of the threshold tone

at that frequency. (It was observed that for tones appreciably lower or higher in pitch than 1,000 d.v., the ratio of the energy of the tone which just excited the sensation of pain to the energy of the threshold tone became much less than $10^{12}$. This may have an important bearing upon the interpretation of threshold curves which are used for determining the sensitiveness of the ear.)

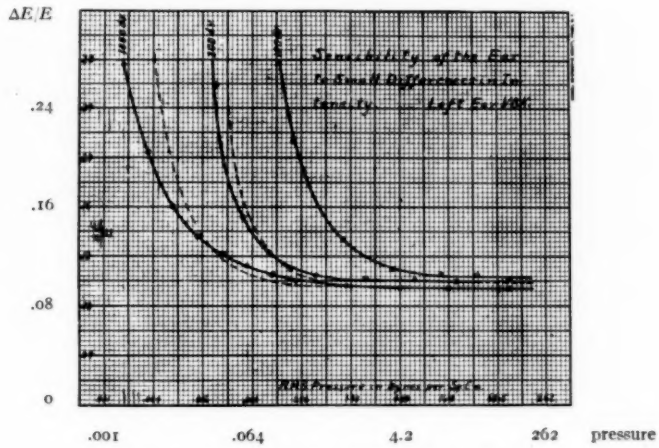



Fig. 4. Intensity Sensibility of the Ear

Fig. 4 shows three of the curves of Fig. 3 with the intensities plotted to an absolute rather than a relative scale. The absolute values of intensity for these curves were computed by giving to the threshold intensities the absolute average values obtained by Fletcher and Wegel [1] from measurements on 41 normal ears. This transformation simply shifts the curves in Fig. 3 along the horizontal axis. As the frequency increases the threshold energy decreases. Consequently of the three curves shown in Fig. 4 the one for 1,000 d.v. is to the extreme left. For decreasing frequency the curves shift to the right.

This group of curves for the ear is strikingly like a similar group of curves for the eye obtained by König and Brodhun and recalculated by Nutting.[2] A reproduction of these curves for the eye, giving the relation between the Fechner ratio for the eye and the intensity of the light, is shown in Fig. 5. It is interesting to note the fundamental agreement of form and position of these two families of curves for the ear and for the eye. The curves for the eye, like those for the ear, shift to the right as the frequency decreases. There is one essential difference between the

[1] The Frequency-Sensitivity Characteristic of Normal Ears, H. Fletcher and R. L. Wegel, PHYS. REV., Vol. 19, p. 553, 1922.

[2] The Luminous Equivalent of Radiation, P. C. Nutting, Bur. of Stds., 5, 261.

Fechner ratios for the ear and eye; namely, the Fechner ratio for the ear approaches the constant value 0.10 at high intensities of sound, whereas the Fechner ratio for the eye approaches the constant value 0.015 at high intensities of light.

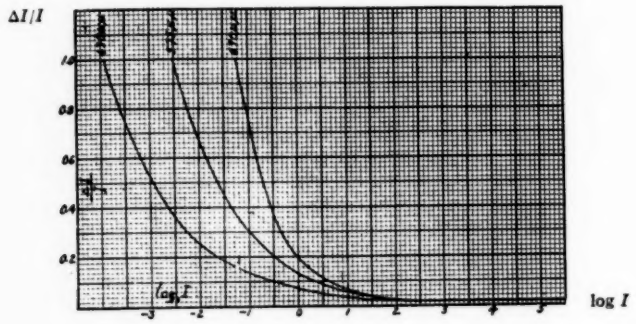



Fig. 5. Fechner Ratio for the Eye as a function of Intensity of Light

2. *Sensibility to Small Differences of Intensity as a Function of Frequency.*—Fig. 6 shows how the sensibility to small differences of intensity depends upon the pitch of tones within the chief portion of the tonal range used in speech and music. The curves are for 19 individual ears from 16 persons. For three persons the curves for both right and left ears are

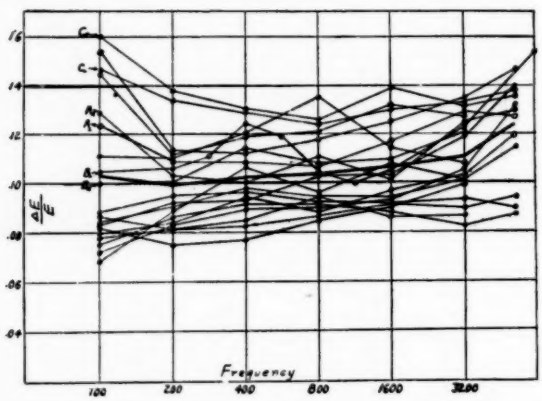



Fig. 6. Intensity Sensibility as a function of Frequency

shown. All of the curves are for people who heard normally well and were experienced in making careful observations. All of the observations were made upon tones of the "same" loudness. The "same" loudness, as here employed, means that the amplitude of the tones used for these tests all bore a constant ratio to their respective threshold amplitudes.

The value of this constant ratio was 100. Such tones are of suitable loudness for making reliable judgments and yet not loud enough to produce serious fatigue effects.

The average curve for the 19 individual ears is indicated by the heavy line. Although the individual curves differ appreciably and in many cases show that the Fechner ratio depends upon the pitch of the tones, the average curve indicates that from 100 d.v. to 3,200 d.v. the Fechner ratio is almost constant, provided that the tones have the same loudness. The value of $\Delta E/E$ over the above-named range is roughly 0.10.

A few measurements were made upon tones of higher pitch than those shown in Fig. 6, but their reliability was questionable because of contact noises which were not entirely eliminated for tones whose frequency exceeded 4,800 d.v. Such measurements as were made, however, indicate that for tones above 5,000 d.v. the Fechner ratio increases appreciably, perhaps to about .20 at 12,000 d.v.

Curves numbered $A_R$, $A_L$, $B_R$, $B_L$, and $C_L$ are for the right and left ears of observers $A$, $B$, and $C$ respectively. These curves indicate that in general the intensity-differentiating mechanisms in a person's two ears are more nearly alike than those in two ears of different persons, although a person's two ears show noticeable differences in this function. See for example the curves for $B$'s right and left ears.

Tests made with binaural hearing showed that within the limits of perceptional error the single ear could distinguish the same percentage change of intensity as could both ears operating together, provided as much energy was fed into the single ear as was fed into both ears. The Fechner ratio for tones of the same loudness was also found to be independent of the mode of generating and receiving the tones. Thus the same value of $\Delta E/E$ was obtained whether the observer listened to a tone produced by the loud speaker receiver, by the double-phone head receivers, or by the König resonators.

The curves shown in Fig. 6 were computed from data which were obtained by the method of minimal change, already described. The observers were required to perceive *only a difference* of intensity and in general were not required to determine the *direction* of the difference. But with a little training it was found that one can nearly always determine the direction of the difference whenever one can perceive that a difference, however small, exists.

To verify this, and also to check the correctness of the data from which the curves in Fig. 6 were obtained, the method of right and wrong guesses was employed for determining the $\Delta E/E$ for five different ears. The two tones whose intensities were to be compared were separated by a

time interval of 1/3 second. Each pair of tones to be compared was presented twice, in the same order, the order of presentation having been determined by previously tossing up a coin.[1] The observer was required to decide or guess whether the first or the second tone sounded the louder.

With the telephone receiver as the source of sound, the method of right and wrong guesses applied to tones whose amplitudes were 100 times their respective threshold amplitudes, gave the following values:

| Pitch | 200 d.v. | 400 d.v. | 800 d.v. | 1600 d.v. |
|---|---|---|---|---|
| $\Delta E/E$ | .118 | .115 | .113 | .106 |

The same method, but with the receiver in front of a König resonator and the ear coupled to the resonator by means of a rubber tube, gave the following values;

| Pitch | 220 d.v. | 400 d.v. |
|---|---|---|
| $\Delta E/E$ | .117 | .108 |

These values agree very well with those obtained by the method of minimal change.

3. *Sensibility to Small Differences of Intensity as a Function of Quality.*— To determine whether the purity of the tone affected the value of the Fechner ratio, measurements were taken on two ears for tones of the same intensity and pitch, but of different quality. The quality was varied by changing the plate resistance of the oscillator circuit. As the plate resistance becomes small the wave-form of the generated a.c. becomes flattened and consequently harmonic overtones are effectively introduced. With a plate resistance of 200,000 ohms, the oscillator tube amplifies almost linearly and therefore the wave-form is nearly sinusoidal. With a plate resistance of only 3,000 ohms, the oscillations are not restricted to the linear portion of the characteristic curve of the oscillator tube, and as a result the wave-form of the generated current differs greatly from a pure sine curve.

The following average values of $\Delta E/E$ for a tone of 200 d.v. were obtained for different values of the plate resistance:

| Plate resistance | 200,000 ohms (pure tone) | 50,000 ohms (fairly pure tone) | 3,000 ohms (impure tone) |
|---|---|---|---|
| $\Delta E/E$ | .114 | .112 | .112 |

Similar data were obtained for tones of 400 d.v. The data indicate that the Fechner ratio is almost independent of quality,

[1] The method of right and wrong guesses used in these experiments is essentially the same as that used by C. E. Seashore at the University of Iowa.

4. *Dependence of $\Delta E/E$ upon the Time Interval.*—The method of right and wrong guesses was further used to ascertain how the Fechner ratio varied with the interval of time between the two tones whose intensities were to be compared. Fig. 7 shows how $\Delta E/E$ varied with the time interval, up to 10 seconds, for five persons. The average curve is indicated by the heavy line. Insufficient individual curves were obtained to give reliably the exact form of the average curve, but even as it is—an average of only five ears—it closely resembles well-known parabolic memory curves.

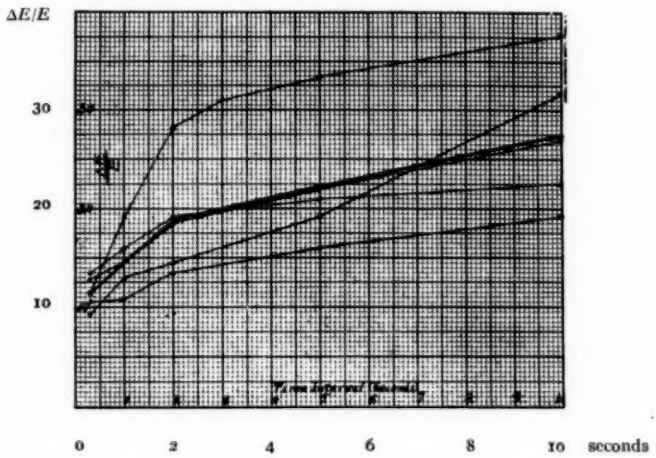



Fig. 7. Variation of $\Delta E/E$ with the Time Interval.

5. *Sensibility to Small Differences of Frequency for Tones of Different Intensities.*—Fig. 8 shows how the sensibility of the ear to small differences of frequency depends upon the loudness of musical tones. The ratio of the smallest perceptible difference of frequency of the tone to the total frequency of the tone, $\Delta N/N$, is plotted against the relative loudness, $I_R/I_0$. $I_R/I_0$, as already defined, means the ratio of the test current in the receiver to the current in the receiver required to produce the threshold intensity. The curves in Fig. 8 show that the $\Delta N/N$ depends upon the loudness in nearly the same way that $\Delta E/E$ depends upon loudness.

The error for separate judgments in determining the liminal difference of pitch is about the same as for discriminations of loudness, namely, about 10 per cent. The uncertainty for either pitch or loudness discriminations is greater for very feeble tones. The curves shown are for the writer's left ear only, but data on other ears exhibit the same general properties. The curves show plainly that the resolving power

is also different for tones of different pitch. This will be treated more fully in paragraph 7.

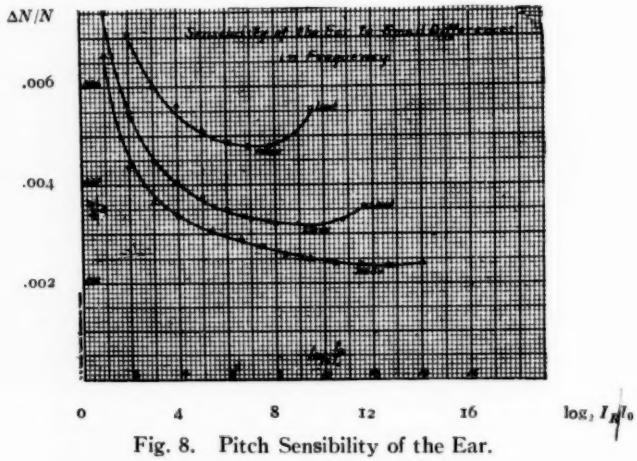



Fig. 8. Pitch Sensibility of the Ear.

6. *Influence of the Mode of Reception upon the Sensibility to Small Frequency Differences.*—The data on pitch discrimination given in the last paragraph are for monaural reception in which the observer holds the single telephone receiver to one of his ears. Tests made on binaural reception indicate that a person's two ears are better than a single ear for appreciating small differences of pitch. The results of some measurements comparing different modes of reception are shown in Fig. 9. Curves I. and II. show that the resolving power for the observer's left ear is nearly the same as for his right ear. Curve III., obtained with

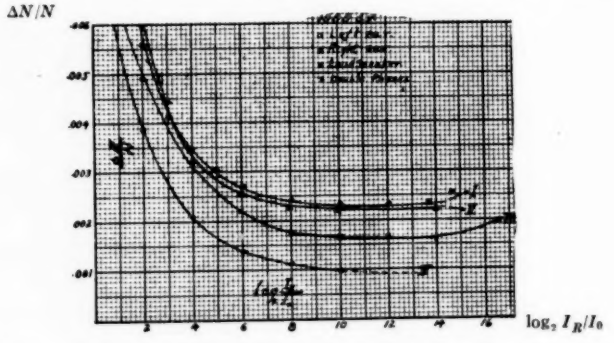



Fig. 9. Influence of Mode of Reception on Pitch Sensibility

double-phone receivers held to the two ears of the observer, indicates that binaural reception enables one to resolve smaller differences of pitch than monaural reception does. Curve IV., obtained with the loud speaker

receiver as the source of sound, apparently indicates that this mode of reception yields a higher resolving power than either monaural or binaural reception with the receivers held to the ears. However, near the barely perceptible change of pitch, it is difficult to determine whether the difference is one of pitch or of loudness. One is prone to judge a slightly louder tone as a tone of slightly higher pitch, and vice versa. It was suspected therefore that the extraordinary results indicated by Curve IV. might be partially attributed to the interference pattern surrounding the ears. Such an interference pattern, caused by reflections from obstacles in the room, would produce at the ears of the observer slight differences of intensity of the two tones compared which at the receiver differed only in frequency. Tests showed that the interference pattern actually did affect the judgment of liminal differences of pitch. Thus at 1,000 d.v. the smallest perceptible difference was first found for binaural reception, using the double-phone head receivers as a source of tone. Then that same difference was produced with the loud speaker receiver. The difference, and in general the direction of the difference, were then clearly perceptible. However, if the observer moved his head to different positions in the room there were definite places where the difference of pitch was no longer perceptible, and still other positions where the direction of the difference was judged reversed, that is, where the graver tone seemed the higher. Hence, where stationary waves are produced, the method of liminal change does not give the true resolving power of the ear, but gives a hybrid resolving power which exceeds the true value because the difference of pitch as heard by the ears of the observer is accompanied by a difference of intensity—the magnitude of the latter depending upon the nature of the interference pattern surrounding the head.

The writer was unable to find any reason for explaining the departure of Curve III. from I. and II. unless it be assumed that binaural reception actually yields a higher resolving power than monaural reception. If such a difference as that shown in Fig. 9 does exist, a careful study of the problem may be helpful in determining the nature of the pitch-differentiating mechanism in the ear.

7. *Sensibility to Small Differences of Frequency for Tones of the Same Loudness but of Different Pitch.*—Fig. 10 shows how $\Delta N/N$ varies with the frequency for 15 different ears from 12 persons. The amplitude of vibration for each test tone was 100 times its threshold amplitude. The tones were produced in the single telephone receiver which was held against the observer's ear. The average curve indicates that $\Delta N/N$ decreases from about .01 at 50 d.v. to about .003 at 600 d.v. From 600

d.v. to 3,200 d.v. it remains at the constant value of about .003. Thus for the intensity of tones employed for these tests the average single ear can just appreciate a difference of 0.5 vib. at 50 d.v., 0.66 vib. at

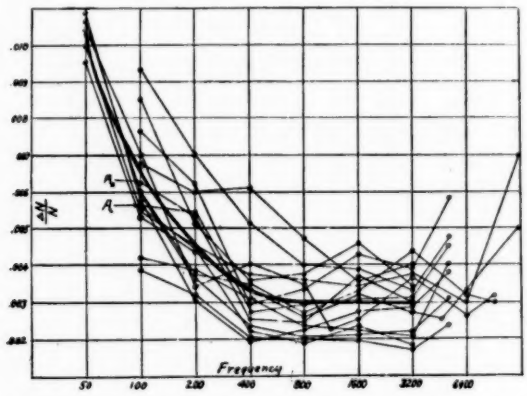



Fig. 10. Variation of Pitch Sensibility with the Frequency

100 d.v., 1.6 vibs. at 500 d.v., 3.0 vibs. at 1,000 d.v., and 9 vibs. at 3,000 d.v. This does not mean that the average untrained ear can distinguish which of the two compared tones is the graver for such small differences. The observers were required to determine *only* a *difference* of pitch. The trained ear can determine the correct direction of the difference for much smaller intervals than the untrained ear. Thus, tests made upon two well-trained musicians showed that as long as they could perceive a difference of pitch of two tones they could also determine which one of the two was the graver. Other people with but little musical ability or training could distinguish differences nearly as small as the trained musicians but these people were not at all certain about the directions of the differences near their just perceptible values.

## V. Discussion of Results.

1. *Comparison of Data with the Results of Previous Investigators.*—The numerical values of $\Delta E/E$ presented in the last section agree fairly well with Wien's value at 440 d.v. and with Deenik's organ pipe values between $c_2$(261 d.v.) and $c_5$(2,088 d.v.). Deenik's higher values of $\Delta E/E$ for tones below $c_2$ may be partially attributed to his working with relatively feeble intensities for the graver tones. The results given in the present paper indicate that $\Delta E/E$ is more nearly independent of the frequency than is indicated by the results of Wien or Deenik.

The data for the resolving power of the ear given in this paper more nearly accord with Stücker's average values than with those of other

investigators. They are in good agreement with Vance's data for tones above 256 d.v. The discrepancies among other investigators, it seems to the writer, can be reasonably attributed to inaccuracies in measuring the frequency, to the presence of higher partial tones, to the differences of loudness of the tested tones, to the presence of sound interference patterns, and to the different time intervals between the two tones whose frequencies are compared.

2. *Modification of the Weber-Fechner Law.*—About sixty years ago G. T. Fechner expressed Weber's law in the mathematical form $\Delta E/E =$ constant. He assumed that the constant $\Delta E/E$ was proportional to the corresponding increment in sensation, $\Delta S$, that is, $\Delta E/E = C\Delta S$. He further assumed that $\Delta E$ and $\Delta S$ were true differentials, and integrating the above expression he obtained the important law of psycho-physics, namely, that the sensation is proportional to the logarithm of the exciting stimulus. Nutting[1] has shown that this is subject to serious defects, and in the case of light sensation has proposed the following form for expressing the Weber-Fechner law,

$$\Delta I/I = P_m + (1 - P_m)\,(I_0/I)^n. \tag{5}$$

This applies quite satisfactorily to low as well as high intensities. $\Delta I/I$ is the Fechner ratio, $P_m$ is the minimum value the $\Delta I/I$ approaches at high intensities, $I_0/I$ is the ratio of the threshold intensity to the total intensity of the stimulus, and $n$ is an arbitrary number depending upon the wave-length.

The $\Delta E/E$ for sound perception can be expressed by a similar equation,

$$\Delta E/E = F + (1 - F)\,(E_0/E)^n, \tag{6}$$

where $F$ is in the constant minimum value the $\Delta E/E$ approaches at high intensities, and $E_0/E$ is the ratio of the energy of the threshold tone to the energy of the tone producing the sensation. This equation satisfies the terminal conditions, for at the threshold $E_0/E = 1$ and therefore $\Delta E/E = 1$, and at very high intensities $E_0/E$ is very small and therefore $\Delta E/E = F$. The dotted curves in Fig. 4 were obtained by plotting the graphs of (6), in which $n$ was the average value resulting from the substitutions of observed values of $\Delta E/E$, $F$ and $E_0/E$ in equation (6). For the 1,000 d.v. curve $n = 1.05$ and for the 200 d.v. curve $n = 1.63$.

The similarity of the sensibility curves for the eye and the ear shown in Figs. 4 and 5 suggests the need of determining the exact form of the

[1] The Luminous Equivalent of Radiation, P. C. Nutting, Bur. of Stds., 5, 261. See also: Sur L'interpretation de la Loi de Weber-Fechner, V. Henri and J. L. des Bancels, C. R. de la Soc. de Biol., 72, 1075–78.

corresponding curves for other sensations, as taste, smell, pressure, warmth, and so forth. If all of these should prove to be similar to the curves for the sensation of light and sound, it might be possible to formulate a general relation between stimulus and sensation for stimuli of all intensities which affect our senses.

The writer is indebted to many of his colleagues at the Ryerson Physical Laboratory who assisted in contributing the data. He wishes to acknowledge the helpful suggestions received from Prof. H. G. Gale, Prof. A. C. Lunn, and Dr. John P. Minton. Finally, he wishes to thank Mr. Walter H. Merrymon, whose coöperation greatly facilitated the experimental work.

RYERSON PHYSICAL LABORATORY,
June 16, 1922.

# VARIATION OF DIATHERMANCY WITH THE TEMPERATURE OF THE RADIATING SOURCE.

By S. Leroy Brown.

Abstract.

**Instrument for measuring radiant heat energy.**—The radiation is focused by a mirror on a thin piece of copper oxide, 1 mm.² in area, with a resistance of 10,000 ohms and a temperature coefficient of resistance of 0.01 per degree. Such an instrument is simple to construct and use and is easily made sensitive to one per cent. of the radiation from a tubular electric furnace at 500° C.

**Diathermancy of various substances to the total radiation from a tubular furnace for temperatures from 200 to 1,200° C.**—For furnace temperatures of 400, 700 and 1,000° the percentages transmitted are as follows: *water* (½ mm.), 4.6, 14.4, 24.8; *ice* (3 mm.), —, 4.6, 15; *rock salt* (11 mm. clear), 85.6, 87, 89; *white mica* (1 mm.), 6, 14, 29; *glass* (1.2 mm.), 10.6, 22, 40. A column of *moist air* 2.5 meters long containing 0.032 mm. of precipitable water absorbed 8.7 and 7.1 per cent. for temperatures of 510 and 850° respectively.

As early as 1833, the experiments of De la Roche and Melloni showed that many substances are very transparent to visible radiation but decidedly athermanous to the longer heat waves. Glass for example transmits very little of the radiation until the source of the radiation is red or white hot; that is, the visible part of the spectrum must be comparatively intense before much radiant energy is transmitted through glass. A few substances like rock-salt are both transparent to the visible portion and diathermanous to the infra-visible portion of the spectrum. A great amount of experimental work on diathermancy with particular attention to pure gases and moist air was done by Tyndall,[1] Magnus[2] and others in the latter half of the nineteenth century and these early experiments indicated that the amount of radiant energy transmitted through the various substances depended on the character of the radiation.

It is the purpose of this paper to describe the results of experiments to determine the per cent. of the total radiation that is transmitted through several substances and to show the variation of the transmission with the temperature of the radiating source. All substances show selective absorption to some extent; and therefore the per cent. of the incident radiation that is transmitted depends on the character of the radiation. The radiation from a furnace becomes richer and richer in the shorter waves as the temperature of the furnace is increased; therefore

[1] "Contribution to Molecular Physics," p. 172.

[2] Phil. Mag., Vol. XXII., 1861.

increased temperature will improve the transmission through substances that are very transparent but not very diathermanous.

The general plan of the experiments was to focus the radiation from a tubular electric furnace on a sensitive electrical resistance element and interpose the substance to be examined between the furnace and the concave mirror which focused the radiation on the resistance element. The concave mirror with polished metal surface does not appreciably change the character of the radiation. The intensity was measured by the change in the electrical resistance of the element at the focus of the mirror, produced by the heating effect. This element is a thin piece of copper oxide about one square millimeter in cross-section, with two connecting wires making electrical connections to the edges of the oxide at

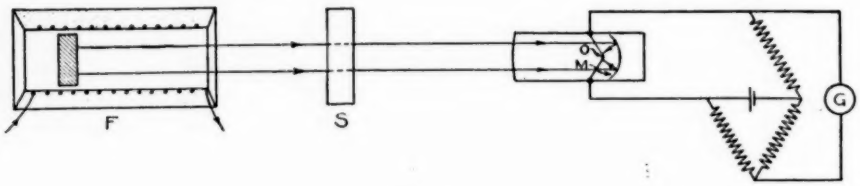



Fig. 1.

opposite sides. The resistance of the element is about 10,000 ohms at room temperature with a negative temperature coefficient of resistance of about .01 per degree. With this oxide resistance forming one arm of a wheatstone bridge, a radiation measuring instrument is thus obtained which is easily sensitive to one per cent. of the radiation from a furnace at 500° C. or one tenth of one per cent. of the radiation from a furnace at 1200° C.

Figure 1 shows the arrangement of the apparatus; *S* is a plate of the material being examined, *F* is a tubular electric furnace, and *M* is the concave mirror focusing the rays from the furnace on the oxide resistance element *O*. The plate *S* was replaced by a stream from a nozzle when water and steam were examined, and the brass tube with rock-salt windows was placed between the furnace and the mirror when the absorption of moist air was measured. The temperature of the furnace was measured with a calibrated platinum-iridioplatinum thermo-couple.

The results show a decided increase of diathermancy with temperature for all substances examined except for clear rock-salt; and even it shows some increase. Glass may transmit not more than 6 per cent. of the total radiation when the furnace temperature is 200° C., 15 per cent. when temperature is raised to 500° C., and 60 per cent. when the furnace temperature reaches 1200° C. White mica transmits only about one per

cent. when the radiating source is at 200° C., but its transmission increases to 40 per cent. when the temperature of the source is raised to 1200° C. Ice and water are decidedly athermanous to the total radiation from a furnace at 400° or 500° C., but may transmit 20 or 25 per cent. when the temperature of the furnace is raised to 1000° C. A thin jet of steam about 1.5 mm. thick does not absorb as much as one per cent. for temperatures ranging from 500° C. to 1000° C. if care is taken not to allow condensation at the surface of the steam in contact with the cooler air. This condensation was prevented by keeping the air in contact with the steam at a higher temperature than the steam. However, a column of moist air 2.5 meters long absorbs about 9 per cent. of the radiation from a furnace at 500° C. The water vapor in the column of moist air which was 70 per cent. saturated at 70° F. was equal to .032 mm. of precipitable water; the thin steam jet, to only .0009 mm.

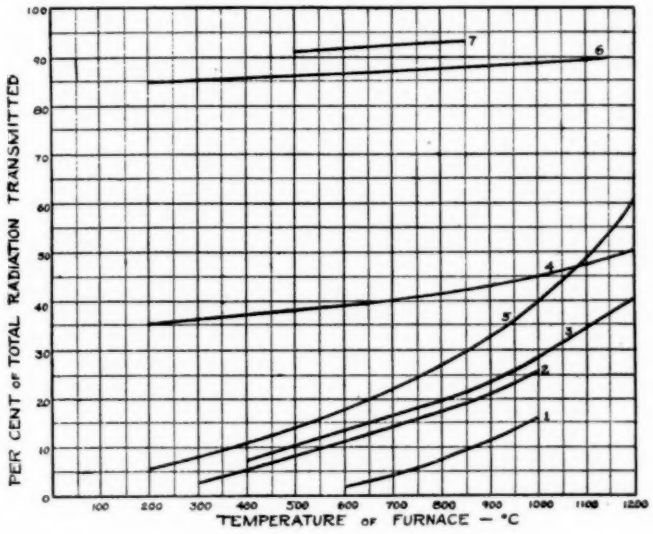



Fig 2.

(1) 6 mm. of ice.
(2) 0.5 mm. of water.
(3) 1 mm. of mica.
(4) 11 mm. of rock salt (dull).
(5) 1.2 mm. of glass.
(6) 11 mm. of rock salt (clear).
(7) 2.5 meters of moist air (70° C., 70 per cent. humidity)

The plan of intercepting the rays with water or steam was to allow a thin stream to flow from a flat nozzle in front of the focusing mirror. Moist air was examined by measuring the increased transmission through a brass tube 2.5 meters long with rock-salt windows at each end when

the air was pumped out of the tube. The tube was evacuated to a pressure of about 5 millimeters.

| Temperature of Furnace, ° C. | Per Cent. Transmitted. |
|---|---|
| *Water (.5 mm.).* | |
| 300 | 2.9 |
| 370 | 4.0 |
| 4 5 | 5.3 |
| 540 | 9.0 |
| 560 | 9.9 |
| 580 | 10.3 |
| 625 | 11.4 |
| 670 | 13.3 |
| 680 | 13.6 |
| 685 | 13.8 |
| 720 | 15.2 |
| 730 | 15.3 |
| 760 | 15.7 |
| 810 | 18.1 |
| 820 | 18.7 |
| 870 | 20.6 |
| 930 | 22.8 |
| 940 | 23.0 |
| 960 | 23.6 |
| *Ice (3 mm.).* | |
| 660 | 3.4 |
| 720 | 5.2 |
| 790 | 7.6 |
| 865 | 9.9 |
| 910 | 11.7 |
| 925 | 11.9 |
| 960 | 14.2 |
| *Mica (1 mm.).* | |
| 350 | 5 |
| 410 | 7 |
| 565 | 12 |
| 770 | 18 |
| 895 | 23 |
| 1050 | 31 |
| 1170 | 39 |

| Temperature of Furnace, ° C. | Per Cent. Transmitted. |
|---|---|
| *Moist Air (.032 mm. Precipitable Water).* | |
| 510 | 91.3 |
| 590 | 92.2 |
| 735 | 92.6 |
| 780 | 92.6 |
| 760 | 92.6 |
| 820 | 92.7 |
| 850 | 92.9 |
| *Rock Salt, Clear (11 mm.).* | |
| 200 | 85.0 |
| 300 | 85.5 |
| 400 | 85.6 |
| 500 | 86.0 |
| 600 | 86.4 |
| 700 | 87.0 |
| 800 | 87.4 |
| 900 | 87.7 |
| 1000 | 89.0 |
| 1100 | 89.5 |
| *Glass (1.2 mm.).* | |
| 200 | 5.8 |
| 290 | 8.0 |
| 360 | 9.6 |
| 475 | 12.5 |
| 540 | 15.6 |
| 660 | 20.2 |
| 700 | 22.0 |
| 810 | 27.2 |
| 890 | 31.0 |
| 975 | 37.5 |
| 1100 | 49.0 |
| 1185 | 59.0 |

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